SYNTHESIS AND DEGRADATION STUDIES OF POLYMER STRUCTURES BASED ON POLYSTYRENE

by:

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Dedicated
to
My Parents

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SUMMARY

This research is concerned with the preparation, characterisation and thermal degradation of various types of homo, bifunctional, metal containing, and linked block polymers based on polystyrene.

A brief discussion about anionic polymers, including polystyrene ionomers based on bifunctional carboxyl-terminated polymer and monovalent and divalent metal ions, is presented in Chapter One. This chapter also reviews briefly the definition and classification of polymer degradation.

Chapter Two presents an introduction to the experimental procedure of the several thermal analysis techniques employed in the present work, with emphasis on thermal volatilisation analysis as a more sophisticated technique. The techniques which were used to identify the degradation products are also briefly described.

The preparation and characterisation of polystyrene made by free radical and anionic routes is considered in Chapter Three. The chapter also includes the preparation and characterisation of functionally-terminated polystyrenes with various end groups and metal salts derived from dicarboxyl-terminated polyatyrene.

The thermal degradation of polystyrenes prepared by anionic and free radical routes is the subject of Chapter Four. Programmed heating experiments were employed to investigate the thermal behaviour of these materials. The volatile degradation products were studied by the GC-MS method. It was found that

there is not much difference in the T_{max} of the homopolymers but a considerable difference is observed in T_{onset}. This chapter also contains the literature review on the thermal degradation of polystyrene.

In Chapter Five, the detailed study of polystyrene volatile products is discussed. It is concluded that most of the volatile liquid fraction in polystyrene degradation depends on reactions of the secondary macroradical formed by backbone scission. The amounts of volatile liquid and cold ring fraction (CRF) products in the degradation of polystyrene samples have been determined gravimetrically under vacuum at 300 ^{o}C. The ratio has been found to fall sharply from a value indicating a predominance of monomer over CRF products, which is dependent on the initial molecular weight of the polymer, and it then becomes approximately constant after 30 % degradation.

The degradation of polystyrene is reconsidered in the light of the new evidence. It is suggested that, initially, intramolecular transfer (which generates CRF products) is impeded by the high melt viscosity and intermolecular transfer (which leads to a fall in molecular weight) is favoured.

Several minor products of degradation were traced to the head to head structures present in sodium naphthalenide initiated polystyrene.

The thermal degradation of a set of polystyrenes having various end groups is considered in Chapter Six. In order to assess the effect of the chemical structure of chain ends on the thermal stability of polystyrene, the isothermal weight loss of polymers of closely similar molecular weights were compared. It is concluded that dihydroxyl-terminated polystyrene is slightly less stable than normal polystyrene and that dicarboxyl-terminated polystyrene is

considerably less stable. The diacid chloride end causes initial destabilisation of polystyrene but after early volatilisation (10-15%), the stability at the main decomposition lies between that of dihydroxyl and dicarboxyl-terminated polystyrenes.

In Chapter Seven, the work deals with the thermal degradation of metal salts (Na, Ca and Zn) of dicarboxyl-terminated polystyrene. The nature of the degradation products and structural changes which occur during decomposition suggest a similar pattern of degradation for these materials. The volatile liquid fraction was studied by GC-MS. The degradation data show that the thermal stability of these metal salts is slightly higher than the dicarboxyl-terminated polystyrene and the thermal stability decreases in the sequence : Na > Ca > Zn.

In the main decomposition, the metal salt polymers behave in a similar manner to normal polystyrene, but appreciable differences exist in the relative amounts of cold ring fraction, in which the metal salts produce higher yields. The main mechanism of degradation seems consistent with the free radical mechanism of normal polystyrene but initially heterolytic scission occurs. As a result of this, metal oxide and carbon dioxide were produced. On exposure to the atmosphere, metal oxide is converted into metal carbonate. The thermal degradation of metal salts of dicarboxyl-terminated polystyrene is a new field with many unanswered questions about the exact nature of the mechanism of degradation.

In Chapter Eight, the preparation, characterisation and thermal decomposition of linked block polystyrenes prepared from diacid chloride-terminated polystyrene is described. It was found that these linked block polystyrene samples are relatively more stable than diacid chloride-terminated polystyrene

and comparable in stability with normal polystyrene.

The weight percentages of cold ring fraction from degradation of linked block polymers, however, are higher than for normal polystyrene, which would be due to additional backbone scission at the linking units.

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CHAPTER ONE

INTRODUCTION

1. HISTORY OF POLYMER SCIENCE

Naturally occurring polymers have been used by mankind for various purposes, since ancient times. The main sources of these polymers were animals and plants.[1] Natural resins and gums have been used for thousands of years.

Nowadays polymers are replacing many natural materials and are truly indispensable substances to mankind, being essential for clothing, shelter, transportation and communication, as well as for the convenience of modern living.

In 1846, the first synthetic plastic reported was cellulose nitrate by Schonbein.[2] Later on Parkes[3] synthesised Parkesine in 1862. Shortly after this cellulose acetate by Cross and Bevan[4] and it was later used to make viscose rayon fibre. In 1907, the first thermosetting resin, "Bakelite" was made.[5] This was made from phenol and formaldehyde. In the early 1909, cellulose nitrate and "Bakelite" were used in plastics industries for making electrical and aeronautical goods.

The true nature of macromolecules only became understood in the 1920s, because of the efforts of Staudinger.[6] He switched from the study of natural molecules to synthesise a series of model polymers, which included polystyrene, polyoxymethylene and polyoxyethylene. He proposed a long-chain structure for polystyrene rubber, and polyoxylmethylene.

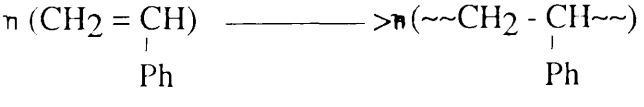
Before that time the prevailing tendency had been to formulate polymeric substances as association compounds held together by partial valencies. The science of high polymers arose in the 1930s, and the major growth of the technology of these materials started even later.[7]

In the period 1929-1938, Carothers[5] produced a range of industrially important polymers and he also developed the basic understanding of the kinetics of the polymerisation and molecular weight distributions. Later on, many organic chemicals were manufactured, including monomers, which are used to make polymers. The rubber, plastic, fibres, coating and adhesives industries are based on natural or synthetic polymeric materials.[8]

1.1. TYPES OF POLYMERIC SUBSTANCES

1.1.1. Definition of Polymer

The term polymer denotes a molecule made up by the repetition of some simpler unit. The structural units may be connected together in various ways. In the simplest of all polymers, the linear polymers, the structural units are connected in a linear sequence, e.g.



Monomer Polymer

1.1.2. Classification of Polymers

In 1829 Carothers[9] classified polymers on the basis of comparison of the structure of the repeating unit of the polymer with the structure of the monomer

and divided all polymers into two types.

1) Condensation Polymers

2) Addition Polymers

1.1.2.1. Condensation Polymers

Condensation polymers[6,7] are those in which the molecular formula of the repeat unit of polymer chain lacks certain atoms present in the monomer from which it is formed.

1.1.2.2. Addition Polymers

Addition polymers are those in which repeated addition of unsaturated monomer units has occurred and the overall composition is that of the monomer unit. Addition polymerisation is known to occur by several mechanisms. The main routes through which usually addition polymerisation occurs are

a) Free Radical Polymerisation

b) Cationic Polymerisation

c) Anionic Polymerisation

1.1.2.2a. Free Radical Polymerisation

Free radical polymerisation occurs basically by the formation of free radicals generated in the presence of a suitable substituted alkene. Addition to the double bond occurs with the generation of another radical, in a chain reaction

mechanism.

1.1.2.2b. Cationic Polymerisation

Cationic polymerisation is a process in which the chain carriers are carbonium ions. Usually a Lewis base or other donor of a proton is presumed to be the effective initiator.

1.1.2.2c. Anionic Polymerisation

Anionic polymerisation was carried out on a commercial scale for many years before the nature of the polymerisation was recongnised, in the production of the Buna type synthetic rubber in Germany and Russia by the polymerisation of the butadiene with sodium or potassium metal as the catalyst. For the first time in 1956, the polymerisation of styrene by sodium naphthalene was recongnised as an anionic chain reaction.

Anionic systems provide a most elegant route for the synthesise of homopolymers and block co-polymers. Since the outstanding feature of homogeneous anionic polymerisation is the absence of any fortuitous chain termination step, this enables these systems to accomplish the following control in the synthesis of polymers.

1) Synthesis of polymers having a predictable molecular weight average, from simple stoichiometry;

2) Very narrow molecular weight distributions approaching, approaching the Poisson distribution, by proper adjustment of initiation versus propagation kinetics;

3) Formation of polymers with functional end groups by selective termination

with appropriate reagents;

4) Synthesis of block co-polymers by sequential addition of different monomers to the different living polymer chain.[10]

In the present research work, most of the polymers were prepared by adopting this route.

1.2. IONIC POLYMERS

An ionic polymer is a polymer which contains both covalent and ionic bonds in its chain or network structure. Such materials include some addition polymers. Systematic study of these materials began with the work of Brown[11] on rubbers and Nielsen[12] on polyacrylates.

The ionic polymers which are soluble in water (containing many salt groups) are called polyelectrolytes. These polymers have great industrial importance, particularly in four main areas, namely water treatment, paper, textiles, and oil recovery.

Polymers which are composed of a hydrocarbon backbone containing pendant acid groups which are neutralised partially or completely to form salts are known as ionomers. In general, the concentration of salt groups may vary but the hydrocarbon backbone is always the majority component.

Ionomers are generally prepared from copolymers having either methacrylic or acrylic acid as one component,[13] whilst the other component is either ethylene or styrene.[14,15]

Part of the present discussion is concerned with the thermal behaviour of

polystyrene ionomers based on bifunctional carboxyl-terminated polymer and monovalent and divalent metal ions. These represent a different class of ionomer in which the ions are at the chain ends or at intervals in the backbone structure.

2. POLYMER DEGRADATION[16-20]

2.1. Definition and Types of Degradation

The term degradation is defined as breakdown of higher molecular weight material to simpler fragments. In polymer chemistry, it is used in a restricted sense to denote polymer deterioration or in a wider sense to include all types of polymer reactions. Polymers have been found to be subject to a number of modifying influences depending on the particular environment. Degradation is induced by light, heat, high energy radiation, oxygen, mechanical stresses, chemical attack and bacteria.

2.2. Thermal Degradation

The ultimate objective of studies of the thermal degradation of polymers is the determination of the mechanism involved. Such studies, however, also provide a lot of information about the materials, which is valuable in relation to their use.

A detailed understanding of how polymers break down on heating is important in the designing and synthesis of new materials to meet new or existing requirements. The threshold temperature for breakdown determines the upper limit of temperature in fabrication and the volatile products of degradation are known in order to guarantee the safety of workers.[21]

Polymer degradation may also be applied to recover monomers from polymers such as (polymethyl methacrylate) and this can only be achieved by finding the

optimum conditions. Another aspect of thermal degradation is detailed analysis of the products. This is of particular interest because of well justified current concern regarding toxicity and flammability.

In a limited number of cases, controlled thermal degradation is important in recycling of plastics waste and it is a synthetic route in the special case of carbon fibre production.

In the thermal degradation of addition polymers, three general types of primary thermal decomposition are observed, namely, depolymerisation, elimination and cyclisation.

2.2.1. Methods of Study

Six or seven methods have been reported[22] for studying the thermal degradation of polymers but the choice of method of study depends upon the objectives, which may differ.

The most widely used method in thermal analysis is thermogravimetry (TG) because of the simplicity of the weight loss method. Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are also used but they are less useful than thermogravimetry.

Thermal analysis is usually carried out with the aid of commercially available equipments.[23-26] Thermal volatilisation analysis (TVA)[27-30] and evolved gas analysis (EGA) are also used for thermal analysis but the former is more generally applicable in the case of polymer degradation studies. Some other methods such as thermomechanical analysis (TMA)[7] and torsional braid analysis (TBA)[22] are less widely used in studies of polymer stability.

3. OBJECTIVE OF THIS RESEARCH

The objective of the work reported in this dissertation is synthesis, characterisation and study of the thermal degradation of a number of polymers based on styrene. These included polystyrene with normal ends, polystyrene with reactive functional ends for coupling with other reagents and Na, Ca and Zn ionomers and linked block polymers based on dicarboxyl- terminated polystyrene.

It was intended to examine the effect of these different structural variations on the thermal stability and degradation mechanism of polystyrene.

CHAPTER TWO

EXPERIMENTAL PROCEDURE AND TECHNIQUES OF POLYMER DEGRADATION

This chapter will illustrate briefly the experimental procedures and techniques, both thermal and analytical, which were employed in thermal analysis. More emphasis has been given to TVA which is the most versatile of the techniques described and allows study of all the products of degradation.

1. THERMAL ANALYSIS

1.1. INTRODUCTION

Since the introduction of modern instrument in 1962 (Du Pout, Perkin Elmer), a variety of methods have been developed to study the thermal degradation of a polymer. Methods of thermal analysis permit the investigation of physical phenomena (e.g. changes in crystallographic properties, melting, sublimation, adsorption) and chemical phenomena (e.g. dehydration, decomposition, oxidation, reduction). The most important and most widely used techniques are TG, DTA and TVA.

1.2. THERMOGRAVIMETRY

Thermogravimetry (TG) is an important technique which allows a polymer sample to be raised from ambient temperature to 1000 ^{o}C, while weight loss is recorded directly as a function of temperature. TG has been used[33] for gas-solid interaction studies to 1600 ^{o}C. TG has been coupled with mass spectroscopy in a number of systems.[34-37] Simultaneous DTA-TG equipment for operation to

1500 ^{o}C has been coupled to a quadrupole mass spectrometer.[38]

The stability of polymer can be assessed and the extent of weight loss at each stage of breakdown can be determined quantitatively. Sometimes the TG curves do not clearly distinguish overlapping processes. These are more readily evident using differential thermogravimetry in which the derivative of the weight loss curve is recorded.

A Du Pout thermoanalyser with model 950 thermobalance was used in this project in all TG experiments. The boat shaped platinum sample holder measured 1 x 0.5 x 0.25 cm deep and the temperature measuring thermocouple was placed 0.1 cm from the holder. The degradation was carried out under dynamic nitrogen atmosphere (60ml/min). Programmed work was carried out using a heating rate of 10 ^{o}C/min, the sample being heated from ambient to 500 ^{o}C, both TG and DTG curves being recorded simultaneously. Isothermal degradation was carried out at appropriate temperatures for various times. Powdered samples of the order of 3-5 mg were used.

1.3. DIFFERENTIAL THERMAL ANALYSIS

A Du Pout thermal analyser was used for DTA experiments at a heating rate of 10^{o}C/min under a nitrogen flow of 80ml/min.

When a polymer undergoes a change in its physical state (melting point, glass transition temperature) or undergoes chemical reaction (cyclisation, dehydration), the temperature difference between sample and reference due to exothermic or endothermic activity in the sample, may be measured and plotted as a function of sample temperature. It is customary to plot endotherms downward and exotherms upward, but this convention is not universally followed.[26]

1.4. DIFFERENTIAL SCANNING CALORIMETRY

Differential scanning calorimetry is a technique similar to DTA which involves measuring the varying energy input required to keep an inert reference and the sample at the same temperature during a programmed heating routine.

For differential scanning calorimetry, individual heaters, located as close as possible to the sample and reference vessels, are provided. When the thermocouples indicate a temperature difference, heat is added to the cooler of the two until temperature equality is restored. The rate of heating required to keep the temperatures equal is recorded as a function of sample temperature. The ordinate of the differential thermogram can then be expressed in units of calories or millicalories per second.[43]

DTA and DSC indicate the temperature regions of occurrence of decomposition processes, but do not distinguish these clearly from physical changes in the sample which also involved absorption or evolution of heat.

It may be said that the most sophisticated equipment available for studying degradation consists of the various instruments for pyrolysis of the polymer. Flash conditions may be used for rapid decomposition at a higher temperature, followed by analysis of volatile degradation products by GC-MS and FT-IR spectroscopy. This method gives considerable data on the products depending on the choice of temperatures, but there is no direct information about threshold temperatures for breakdown or number of stages, which is easily provided TG, DTA and DSC.[21]

In the methods consider so far, the products are not collected. An experimental approach widely applied to polymer degradation studies, in which the products are also collected, is Thermal Volatilisation Analysis (TVA).

1.5. THERMAL VOLATILISATION ANALYSIS

Thermal volatilisation analysis (TVA) is a versatile thermoanalytical technique developed in Glasgow University Chemistry Department by McNeill and co-workers.[28,30,39,40] This technique has been used extensively throughout the work. A full description of the equipment and its operation is given below.

1.5.1. Principle of TVA

In TVA a polymer is subjected to programmed or isothermal heating under vacuum and the volatile products are continuously pumped from the heated sample. The volatile products pass to a cold trap and the response of a Pirani gauge placed between sample and cold trap is recorded continuously as a function of temperature. The Pirani response is a measure of the rate of the volatilisation of the sample.

The basic principle of a TVA is illustrated schematically in Fig. 2.1, in which a Pirani gauge is placed between the heated sample and the cold trap (-196 ^{o}C). A modification to the apparatus involves placing a second cold trap B, at a temperature higher than that of the original, A, between the sample and the Pirani gauge as shown in Fig. 2.2. Thus arises the possibility of differential condensation of the degradation products between the two traps. Consequently, this form of TVA is known as differential condensation TVA.

By running a series of experiments each with different first trap temperature, much information about the volatility of degradation products can be provided from comparison of the several TVA traces. However, the form of the apparatus currently used in present work is that illustrated in Fig. 2.3, in which a number of limbs, each with an initial cold trap and a main trap -196 ^{o}C, are joined in parallel. The initial trap temperature differs from one limb to another and 0^{o},

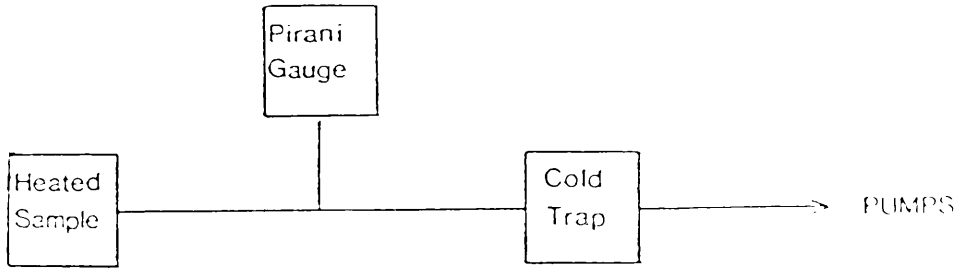
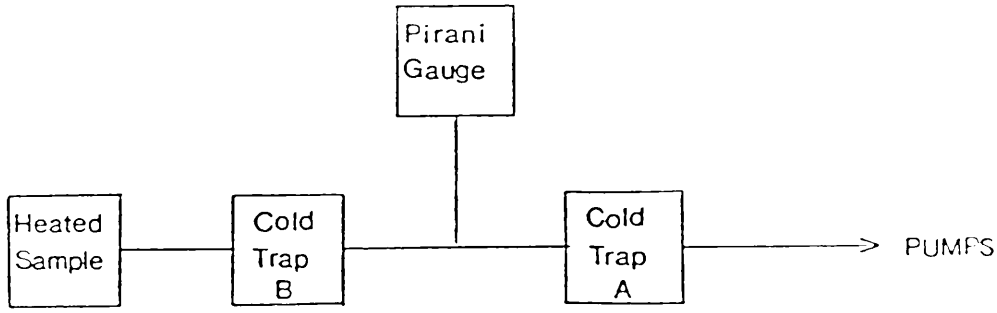


Fig. 2.1. Schematic representation of Basic TVA System.



$$T_B > T_A$$

Fig. 2.2. Schematic representation of Differential Condensation TVA System.

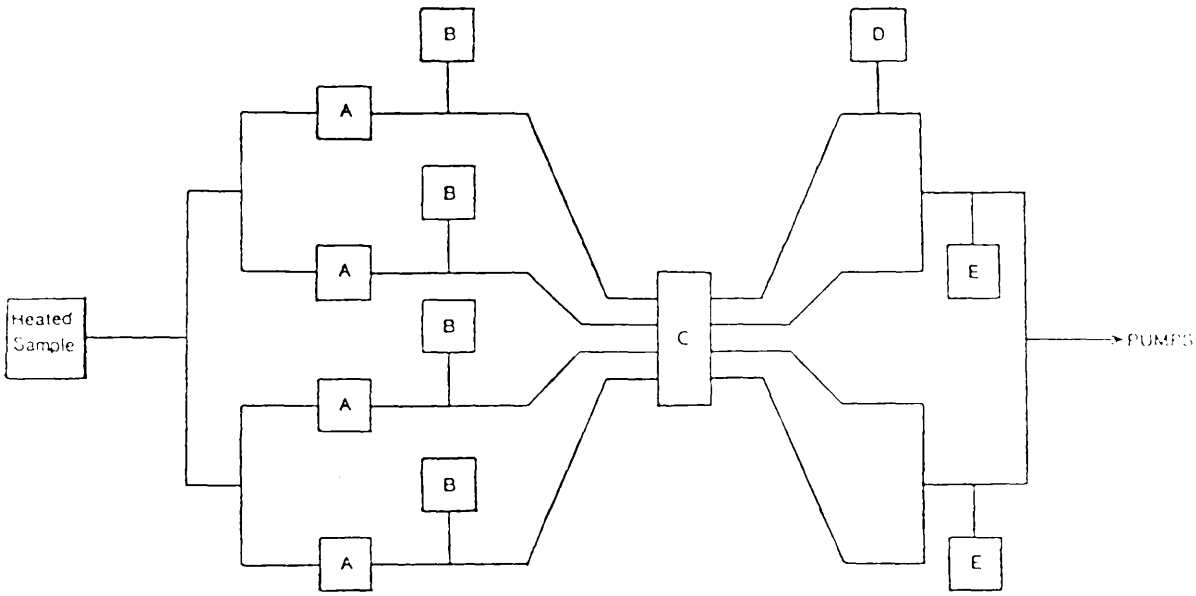


Fig. 2.3. Parallel Limb Differential Condensation TVA System

A = 0^{o}, -45^{o}, -75^{o}, $-100\ ^{o}C$ traps

B, D = Pirani gauges

C = $-196\ ^{o}C$ trap

E = Sample take off points

-45°, -75 °, and -100 °C have been found convenient for polymer degradation. The Pirani gauges placed after each initial trap monitor the passage of volatile materials through the traps as in the basic differential condensation TVA arrangement, and the addition of a Pirani gauge after the -196 °C trap allows the detection of any non-condensable products which are lost to the pump.

The polymer is used in the TVA system in the form of a fine powder or a thin film. Fig. 2.4 shows, diagrammatically, the oven and degradation tube assembly of a typical TVA

line. A Perkin Elmer F-11 gas chromatograph oven has been modified to take the tube assembly and to work to a maximum temperature of approximately 500 °C. The oven can be operated isothermally or with linear increase of temperature in the range of 1 ° to 40 °C/min. Oven temperature is recorded as a millivolt output along with that of the Pirani gauges, using a Leeds-Northrup "Speedomax W" 12 point strip chart recorder.

The pumping system comprises an Edwards Speedivac EO1 oil diffusion pump, backed by an Edwards Speedivac ED 100 rotary pump. Using this system, pressures of 10^{-5} torr are obtainable. Edwards G5 C2 Pirani gauge heads with Pirani model 11 or 14 control units are employed to measure pressures. As TVA in the present form involves the comparison of the output of the five Pirani gauges attached to the vacuum lines, it is essential that the outputs are matched. The output from a Pirani gauge attached to a TVA line depends, for a constant pressure and gas composition, on the exact position of the gauge and the characteristics of the gauge itself. Thus, it is necessary to cross calibrate the gauges. This is done as follows.

First, the line is prepared for a TVA run with all traps in place and pumped to high vacuum. The Pirani gauges are set on zero against the "sticking vacuum" of

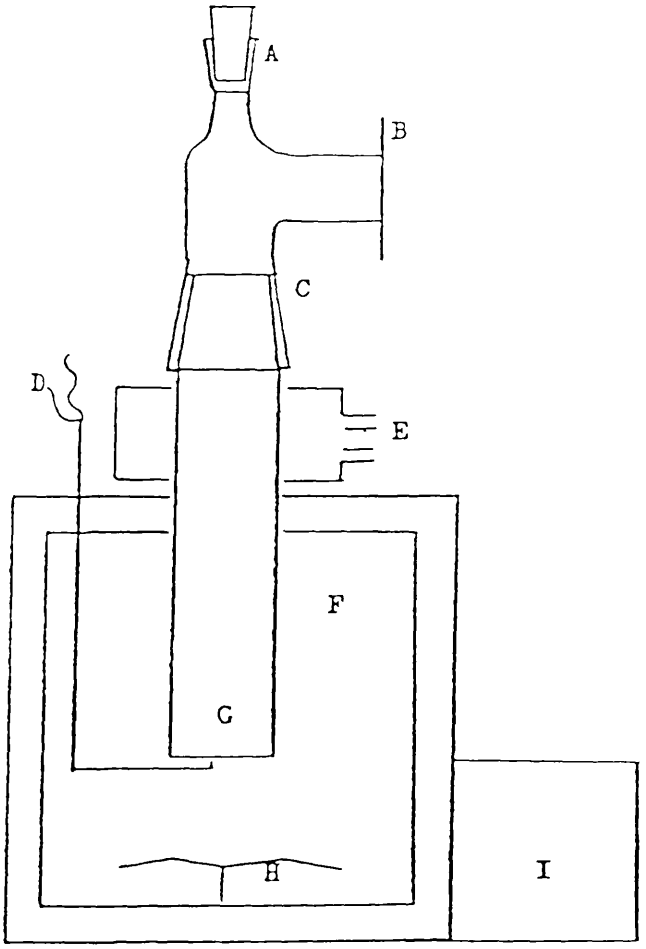


Fig. 2.4. Oven and Degradation Tube Assembly;

A= B19 socket

B= Ground glass flange joint

C= B40 ground glass joint

D= Type K thermocouple

E= Water cooled jacket "cold ring"

F= Oven

G= Degradation tube

H= Fan

I= Programming module

a Vacustat gauge. The line is isolated from the pumps, dry nitrogen is introduced and the line reopened to the pumps until a Pirani output of approximately half a full scale (the maximum usually achieved during a degradation) is recorded. The outputs from the Pirani gauges to the recorder are then brought into coincidence by means of variable resistances. The line is then pumped down in steps, the coincidence of the output being checked at each stage. A final check is made by degrading a sample of potassium permanganate. This evolves oxygen which at the reduced pressure in use is non-condensable at -196 ^{o}C and thus passed through all five traps, the Pirani gauges should then all register the same output.

The Pirani gauges are only linear over a range of 0-2 mv whilst the usual sample size (about 50 mg), on degradation gives rise to an output of up to 5 mv. Further more, the output is dependent on the nature of the gas as well as the absolute pressure, so that for quantitative analysis of degradation products, calibration curves must be constructed.

In the TVA curves obtained in this work, the following designation for the individual trap traces is employed as standard.

_____ 0 ^{o}C (and colder traps if coincident)

..... -45 ^{o}C (and colder traps if coincident)

- - - - - - - -75 ^{o}C (and colder traps if coincident)

_ _ _ _ -100 ^{o}C (and colder traps if coincident)

_ . _ . _ -196 ^{o}C

1.5.2. TEMPERATURE CALIBRATION

The temperature recorded during the TVA experiment is that of the fixed thermocouple below the base of the degradation tube as shown in Fig. 2.4. This is always higher than the actual temperature of the interior of the base of the degradation tube.

The exact decomposition temperature occurring at the tube base can be obtained by calibration using a second chromel-alumel thermocouple, the junction of which is surrounded at the point of contact with the glass base of the tube by a small bead of Apiezon L grease to improve thermal contact.

The system is then evacuated and the blank tube heated to 500 ^{O}C as in a normal TVA experiment. The corresponding temperatures for both oven and sample are simultaneously recorded as shown in Fig. 2.5. Such curves have to be obtained for each tube and have to be repeated whenever an alteration in the position of the oven thermocouple or rewiring may alter the calibration.

1.5.3. MODIFICATION IN THE TVA APPARATUS

In the present work two approaches have been used - programmed heating at 10^{O}C/min and isothermal heating at appropriate temperature for various times. Fig. 2.4 shows the apparatus which was used for programmed heating. Some modifications were carried out in the degradation tube arrangement of the TVA apparatus for isothermal heating, as shown in Fig. 2.6. The total volatile products (CRF + liquid fraction) were efficiently collected on the cold finger during degradation and subsequently be weighed. The small sample bottle was in contacted with the TVA tube during degradation and it also increased the accessibility for quantitative measurement of residue.

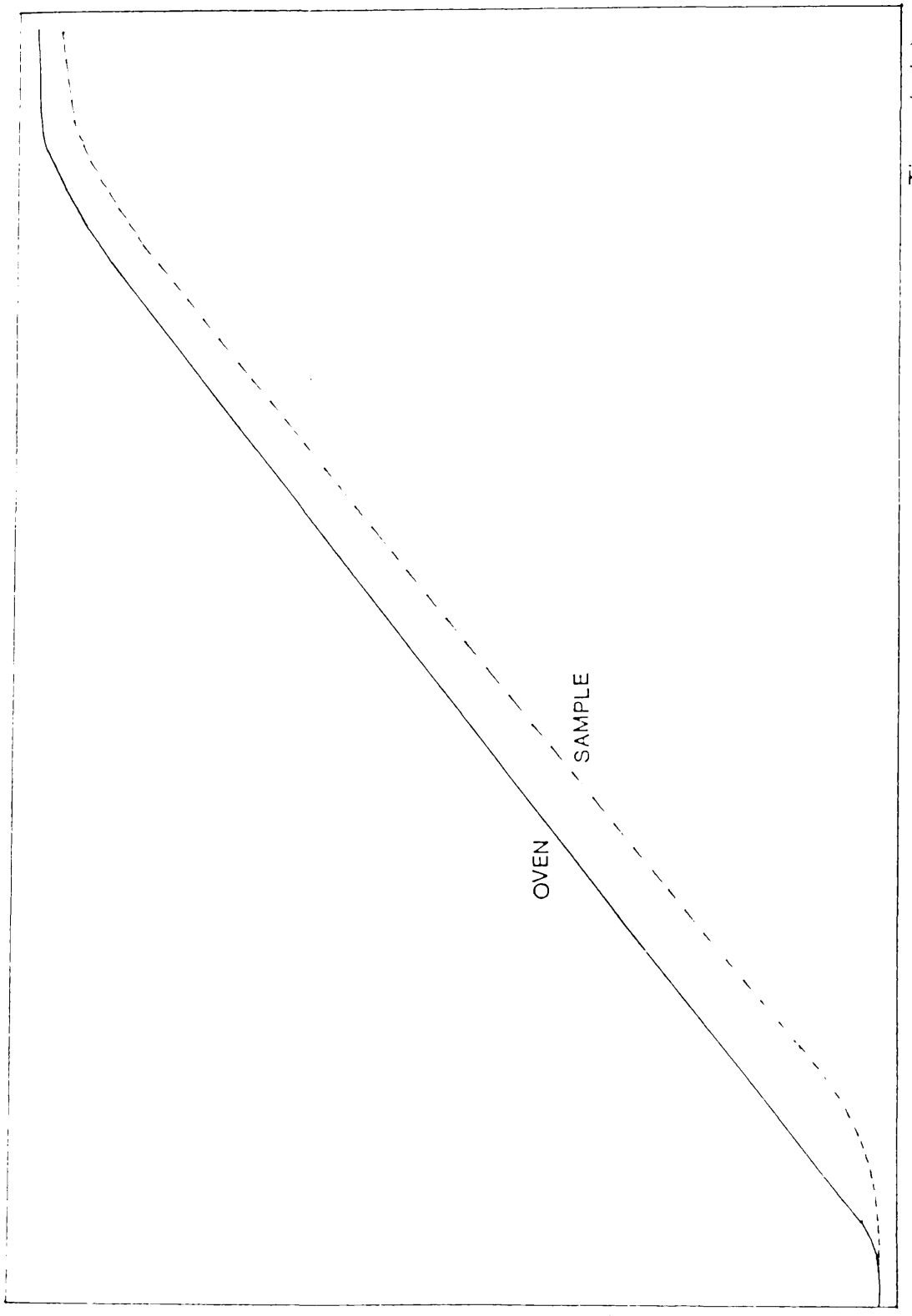


Fig. 2.5. Tube Temperature Calibration Chart.

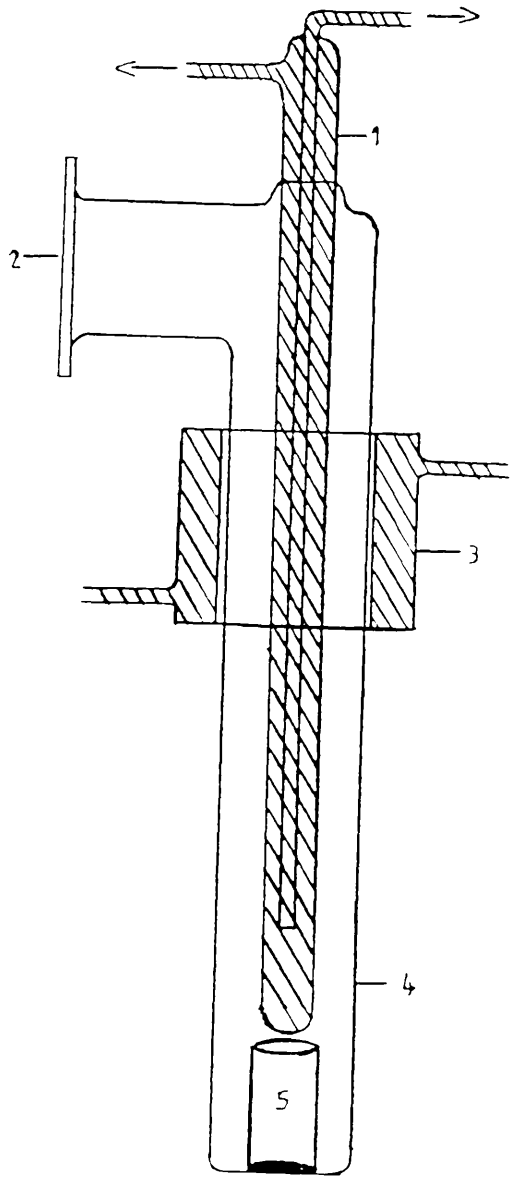


Fig. 2.6. Modified Degradation Tube Arrangement of the TVA Apparatus;

Keys: 1; Cold finger, 2; flang connection to vacuum system, 3; cold ring, 4; degradation tube, 5; sample tube.

1.5.4. Product Analysis

The great advantage of the TVA apparatus is that the various product fractions from degradation of a polymer are available for further study, e.g. by spectroscopic methods.

The products arising from degradation of a polymer sample in the TVA apparatus can be divided into two main categories.

a. Involatile Residue

b. Volatile Products

1.5.4a. Involatile Residue

The involatile residue remains on the tube base and is usually insoluble. Residues were analysed by infrared spectroscopy by forming a KBr disc or Nujol mull.

1.5.4b. Volatile Products

The volatile products can be further divided into three classes;

1. Products which are volatile at the degradation temperature, but involatile at ambient temperature, were collected at the top of the degradation tube and referred to as cold ring fraction (CRF). The cold ring fractions were removed for analysis by swabbing with a tissue soaked in a suitable solvent.

2. Substance volatile at degradation and ambient temperature but condensable in a cold trap at -196 ^{o}C, called condensables, can be separated by Subambient Thermal Volatilisation Analysis (SATVA) examination (this technique is

considered in detail in section 1.7.), and transferred to gas cells or cold finger tubes as shown in Fig. 2.7 and 2.8, respectively, for analysis by infrared spectroscopy, mass spectrometry or gas chromatography.

3. The products volatile even at liquid nitrogen temperature (-196 ^{o}C) called non-condensable gases, such as hydrogen, methane and carbon monoxide, can be studied by means of degradation in a closed system followed by collection in a gas cell using a Toepler apparatus.

1.6. TOEPLER LINE

The Toepler line is a useful tool through which gaseous products non-condensable at -196 ^{o}C, evolved from degradation of polymers under TVA conditions, were collected and characterised by spectroscopic methods. The schematic layout of the Toepler line is illustrated in Fig. 2.9.

The polymers were degraded in a sealable tube as shown in Fig. 2.10. The sample was inserted into the base of one limb of the tube which was then connected to the vacuum line. While the tube was continuously evacuated, the constriction was sealed. It was then placed in an oven which was heated under normal TVA conditions. Meanwhile the other limb of the sealed tube was surrounded by liquid nitrogen. When the degradation was completed the sealed tube was removed from the oven and a small magnetic bar was inserted. The tube was then connected to the Toepler line through the socket 8 as shown in Fig. 2.9.

A gas cell was connected to the Toepler line at point 7 in Fig. 2.9 and the whole system was evacuated by opening all stopcocks to the pumps. Once a high vacuum was obtained, stopcocks 3 and 5 were closed and the system was isolated from the pumps. The break-seal was broken using the magnetic bar and any non-condensable gaseous products were released into the system. These

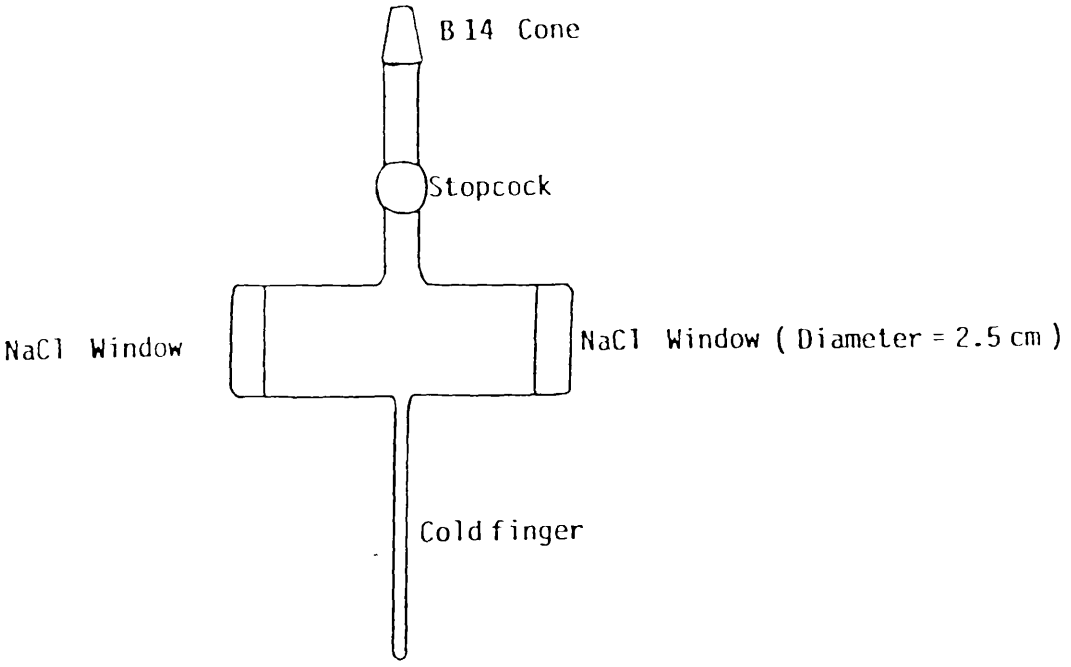


Fig. 2.7. Gas cell for IR and MS analyses.

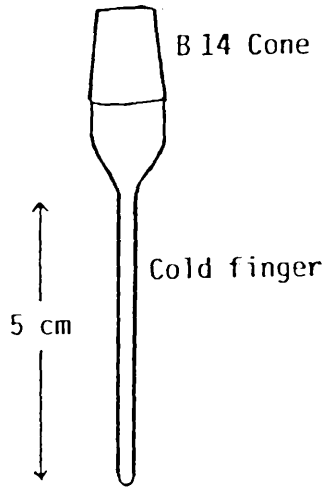


Fig. 2.8. Cold finger for Collection of Liquid Fraction of Degradation Product.

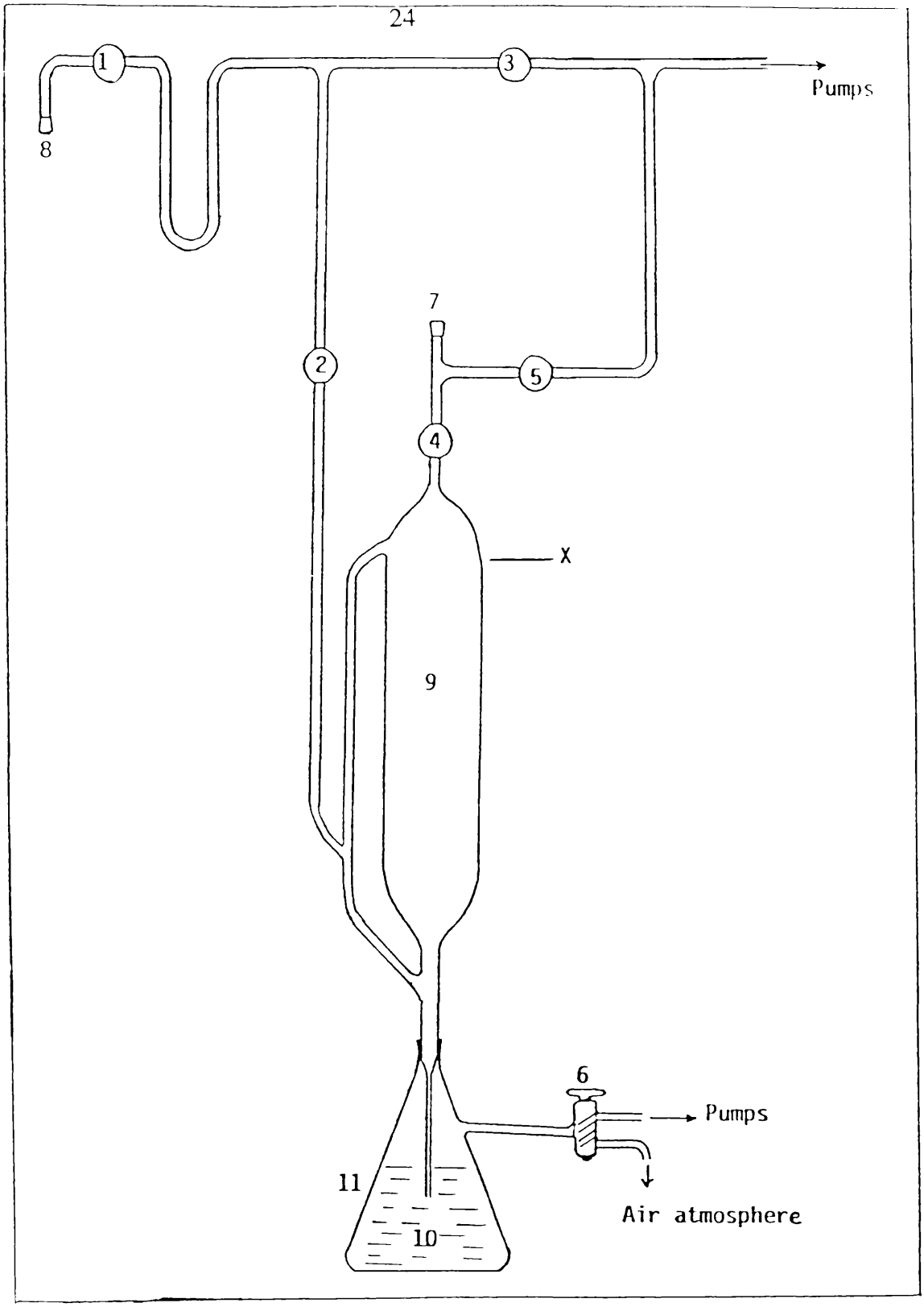


Fig. 2.9. Schematic Layout of the Toepler Apparatus.

Keys: 1-5; stopcocks, 6; two way stopcock, 7; B14 socket for gas cell, 8; B14 socket, 9; reservoir, 10; mercury, 11; conical flask.

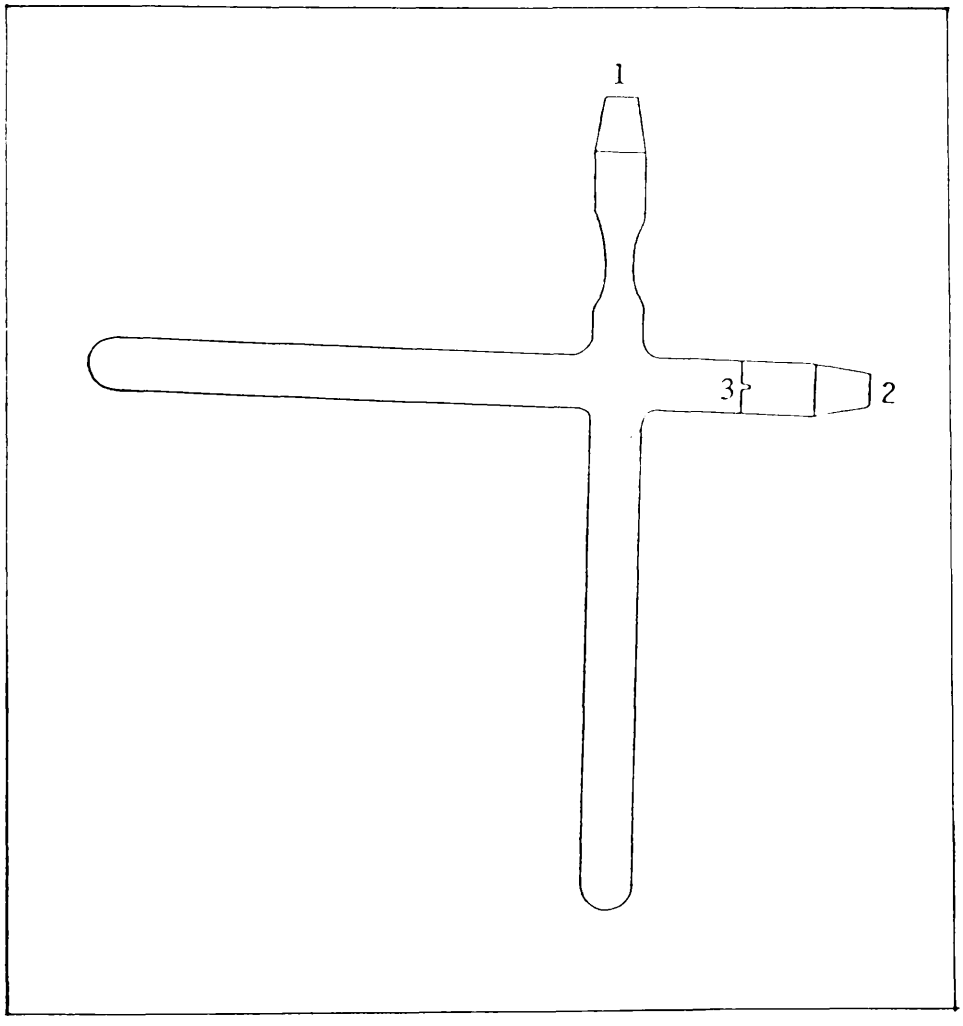


Fig. 2.10. Sealable Tube. 1 and 2; B14 cone, 3; break seal.

products were compressed into the gas cell by adopting the following procedure.

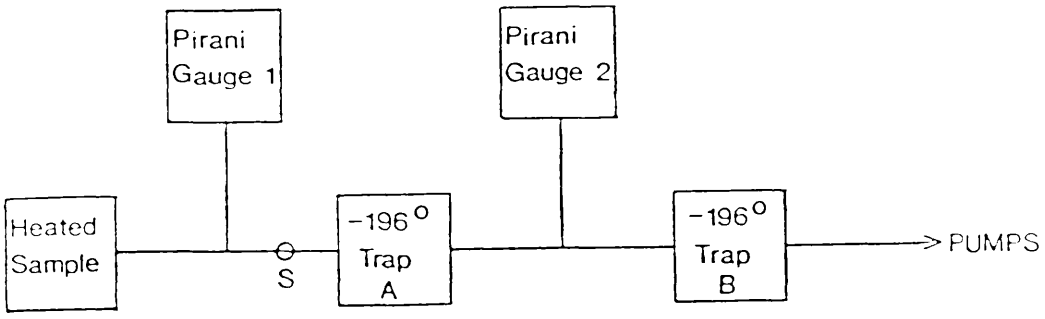
The stopcock 2 was closed and the two way stopcock was opened to atmospheric pressure, which caused the mercury to rise up into the reservoir from the conical flask. As the mercury level rose, the gases were compressed into the gas cell. When the mercury level reached level X (Fig. 2.9) the two way tap was closed, and stopcock 4 was also closed simultaneously. The two way stopcock was then opened to the pump. When this was done the mercury level fell in its original position. The isolated products were collected into the gas cell and it was detached from the Toepler line and characterised.

1.7. SUBAMBIENT VOLATILISATION ANALYSIS

The degradation products released in a TVA experiment, which are volatile at ambient temperature and condensable at -196 ^{o}C, can be further separated into different fractions. The technique through which these products are separated, was developed for use both in thermal and photodegradation studies by McNeill et al.,[29] who refer to it as subambient TVA, (SATVA). This approach has also been used by Ackerman and McGill,[41] who refer to it as differential distillation and applied it to the products of photodegradation experiments only.

The basic principle of a SATVA system is shown in Fig. 2.11. The degradation products from the heated sample are collected in the liquid nitrogen, trap A, the entire system being continuously evacuated. The evolution of the products from the sample can be monitored on Pirani 1, as in a TVA experiment, whilst Pirani 2 may be used to monitor those non-condensable products which pass through the trap and are thus lost to the pumps, unless bled to a mass spectrometer.

The subambient trap (A) is shown in Fig. 2.12. The U-tube is surrounded by a pyrex glass vessel containing beads. The glass vessel is itself surrounded by



S = Stopcock

Fig. 2.11. Principal Features of a SATVA system

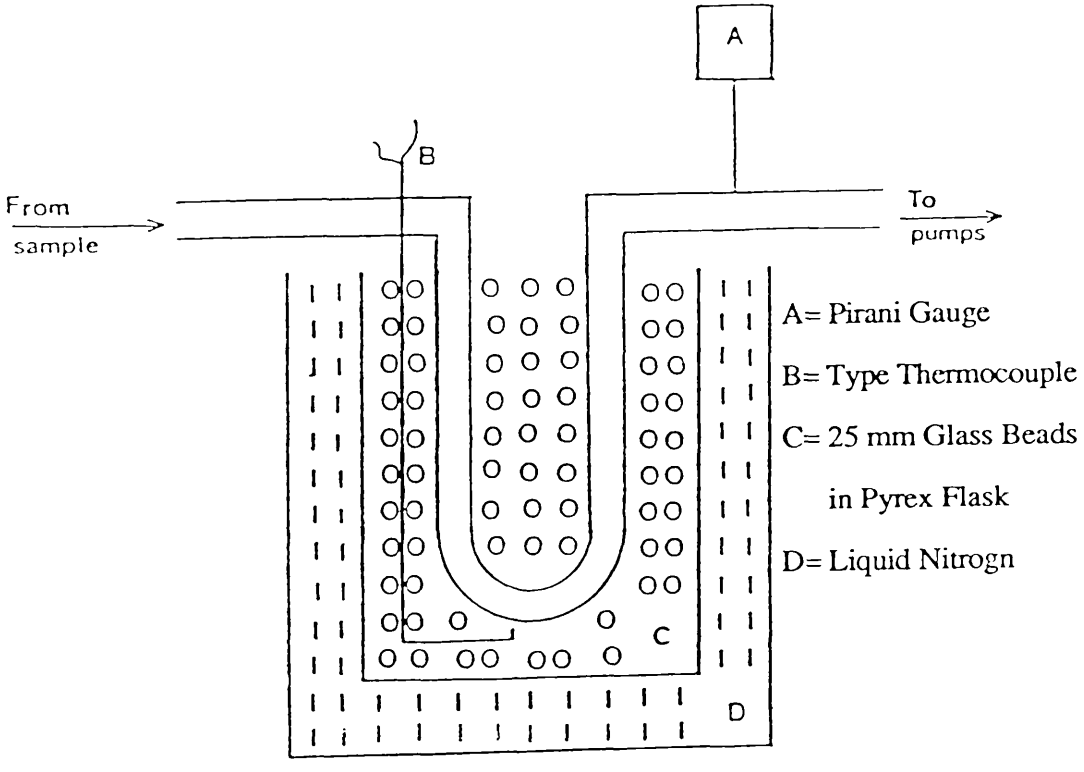


Fig. 2.12. Subambient Trap.

Dewer flask containing liquid nitrogen. A thermocouple measures the temperature of the U-tube.

When the collection of products has been completed, the stopcocks of Fig. 2.11 are closed and the liquid nitrogen removed from around the ambient trap A. The trap will now begin to warm up to ambient temperature. As the trap warms, each of the condensed products will vapourise in turn according to the volatility of the material concerned. The pressure changes associated with the distillation of the products from trap A to trap B are measured by Pirani 2. Both Pirani output and trap temperature are recorded as a function of time.

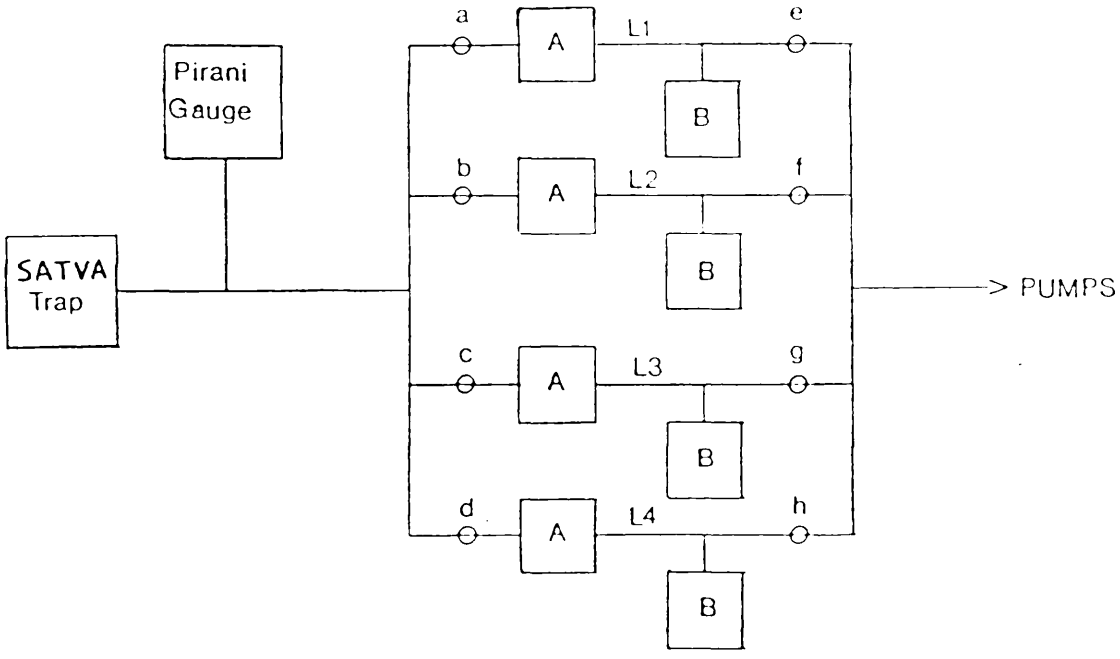
In general, longer warm up time enhances the resolution of the peaks although complete separation of products may not be attained. Isolation of the products giving rise to a specific SATVA peak may be achieved by omitting trap B of Fig. 2.11 and linking SATVA trap A directly to a system such as that illustrated in Fig. 2.13. Initially, taps b, c, d are closed and so any product distilling from B will pass down limb 1 and be condensed in the liquid nitrogen trap A.

When the peak corresponding to this product the SATVA trace has reached a minimum, tap b is opened and a and e are closed. Thus, the first peak product(s) are isolated in the limb 1 whilst the second peak product(s) are collected in limb 2. Similarly, further products may be collected in limbs 3 and 4. Once the products have been isolated, they may be removed for analysis by distilling the material from the -196 ^{o}C trap to an evacuated sample collection vessel.

2. ANALYTICAL TECHNIQUES

2.1. INFRARED SPECTROSCOPY

Infrared spectra were recorded either on a Perkin Elmer grating spectrometer, a



L1 - L4 = Limbs 1-4

A = -196 ^{o}C Trap

B = Take-off point

a - h = Stopcock

Fig.2.13. System Employed for Isolation of Products via SATVA.

Perkin Elmer 983 with P.E. 3600 data system or a Philips PU 9800 FT-IR instrument.

Spectra of polymers and involatile residues of degradation products were run as KBr disc. Gas cells equipped with 25 mm NaCl windows as shown in Fig. 2.7 were used to obtain spectra of gaseous degradation products at room temperature.

The IR spectra for liquid degradation products were obtained by placing a film between two NaCl windows. CRF spectra were obtained by dissolution in a suitable volatile solvent and casting a film onto a salt plate (NaCl). The identification of degradation products from their IR spectra was based on comparison with spectra of authentic samples.[42]

2.2. PROTON MAGNETIC RESONANCE SPECTROMETRY

All spectra were obtained on a Perkin Elmer R32, 90 MHZ spectrometer with signal locking, integeral and spin decoupling facilities. The spectrometer proble was at all times thermostated at 35 ^{o}C.

Chloroform ($CDCl_3$) was used as solvent and tetramethylsilane (TMS) was used as internal reference.

2.3. MICROANALYSIS

Elemental analysis for carbon, hydrogen, and chlorine were obtained using a Caro Erba Elemental Analyser, model 1106.

2.4. ATOMIC SPECTROSCOPY

2.4.1. Atomic Absorption Spectroscopy

Atomic absorption spectroscopy is a very sensitive technique for elemental analysis. The sensitivity is defined as the concentration of an element in µg/ml (or ppm) which produces a transmittance signal of 0.99 or corresponding absorbance signal of 0.0044. A Perkin Elmer 370A spectrophotometer was used for calcium and zinc metals analysis.

2.4.2. Flame Photometry

Atomic emission spectroscopy or flame photometry has found[43] wide spread application to elemental analysis. Its most important uses have been in the analysis of sodium, potassium and lithium. In this study a Perkin Elmer 360A flame photometer was used for sodium metal analysis.

2.5. MASS SPECTROMETRY

In this study, a modified resolution low Kratos MS 12 mass spectrometer with a Micromass DS55 data handling system and a high resolution Kratos MS9025 mass spectrometer with a Micromass DS90 data handling system were used for identification of degradation products.

In addition, a VG Micromass QX 200 quadrupole mass spectrometer coupled with directly to the TVA-SATVA system was occasionally used. In the VG Micromass instrument, compounds with a molecular weight less than 200 a.m.u. could be analysed. Non-condensable gaseous products evolved from the degradation were bled into the mass spectrometer during the heating process. In addition, condensable products may be fractionated by SATVA and samples at each peak may be admitted to the mass spectrometer as they are evolved.

2.6. GAS CHROMATOGRAPHY - MASS SPECTROMETRY

In this study, volatile liquid products from the degradation of a polymer were separated by using a Perkin Elmer Sigma 3 chromatograph interfaced to a Kratos MS 30 mass spectrometer with DS90 data handling system.

Excellent results have been obtained by using this technique. The different columns which were used for the separation of the volatile liquid products are given in Table 2.1.

2.7. GEL PERMEATION CHROMATOGRAPHY

Number-average molecular Weight ($\bar{M}n$) of polymers were obtained as a service from the Polymer Supply & Characterisation Centre. The following conditions and columns were used.

Columns	P.L. gel	1×10^3 A
		1×10^4 A
		1×10^5 A
		1×10^6 A
Solvent	Tetrahydrofuran, stabilised with 2,6,di-tert-butyl-p-cresol	
Flow rate	1.0 ml/min	
Temperature	Ambient	
Calibration	Third order polynomial, using polystyrene standards	
Detector	Viscosity, refractive index	

Table 2.1 Columns used for the Separation of Volatile Liquide Degradation Product.

Colunm	BP-10	DB-5
Column packing	14% Cyanopropyl-dimethylsiloxane	5% Phenyl silicone
Polarity	Slightly polar	Polar
Length (mm)	25.0	15.0
Inside diameter(mm)	0.330	25.0
Film thickness(μm)	0.50	1.0
Gas carrier	He	He

2.8. VISCOMETRY

Molecular weight were also determined by using a U-tube viscometer such as the "Desreux Bishoff" viscometer. The capillary diameter was 0.5 mm and toluene was used as a solvent at 25 ^{o}C. Average molecular weights were calculated from viscometry data at several solution concentration using the Mark- Houwink equation.[44]

CHAPTER THREE

POLYMER PREPARATION AND CHARACTERISATION

The materials under investigation in this work included free radical and anionically prepared polystyrene with normal end structures and functionally terminated polystyrenes. Polymers made by coupling functionally terminated polystyrene with 2,2̄-dihydroxyl-4,4̄-dimethoxybenzophenone and 1,6-diaminohexane, were also examined.

In this chapter a literature review concerned mainly with defining the optimum conditions of anionic polymerisation is first given. There follows a description of the apparatus developed in this laboratory and an outline of the procedure for polymerisation and purification. Finally techniques for characterisation of the polymers are considered.

1. INTRODUCTION

When Scott[45] first used sodium naphthalenide as an initiator in polymerisation, he founded that a green solution of sodium naphthalenide was effective in initiation a very rapid polymerisation of styrene. Scott and co-workers[46] inferred that this complex is a dicarbanion, since they obtained dicarboxylic salts from the reaction with carbon dioxide.

Sodium naphthalenide was later studied as a polymerisation initiator by Whitby and Stephens[47] who were able to polymerise butadiene and isoprene to relatively low molecular weight. They noted that brightly coloured solutions were obtained, red for styrene, orange for diene, but that the colours faded slowly, presumably

because of interaction with atmospheric gases.

Szwarc, Levy, and Milkovich[48] by working under more rigorous conditions, were able to elucidate the mechanism involved in the anionic polymerisation of styrene. The absence of a termination step[49,50] resulted in the system eventually reaching an equilibrium state. The molecular weight distribution would, on theoretical grounds, be of the Poisson type. The most important characteristic of this type of distribution is that the heterogeneity index, defined as $\bar{M}w/\bar{M}n$, can be made very close to one in polymers taken to a high conversion per initiating site. It has been shown statistically[49,50] that to minimise the heterogeneity index of the material, batch addition of monomer is preferable to slow or dropwise addition, provided that polymerisation is slow enough to enable reagent homogeneity to be attained before quantitative consumption of monomer. The depropagation reaction[51] and reactive impurities in the monomer have also been shown to enhance the "most probable" distribution of the polymer more effectively in continuous addition as opposed to batch addition.

It has been reported that absorption bands in the spectrum of sodium polystyryl in tetrahydrofuran show a maximum at 343 mμ. This could be attributed to UV absorbance of the living chain end chromophore. It has also been observed[53] that some unexpected changes occur in the solution of living polystyrene, when it is allowed to stand for a few days. Apparently the 343 mμ peak disappeared and a new peak appeared in 545 mμ region. This was explained by irreversible isomerisation, producing new and stable ions which do not propagate the polymerisation of styrene.[53]

The choice of solvent has a great effect[54] on the course of polymerisations directed at producing narrow distribution polymers. Solvents promoting rapid initiation and relative slow propagation were best, and those promoting the reverse situation tended to give side reactions leading to termination and a broad distribution polymer. Dioxane was more effective in promoting rapid initiation

and slow propagation than tetrahydrofuran.

In dioxane, living polystyrene exists in the form of a $\sim\sim^{-}CHPh, M^{+}$ ion pair. The presence of free $\sim\sim^{-}CHPh$ ions could not be detected, due to the low dielectric constant of this solvent.[55] The dielectric constant for THF is 7.4 compared with 2.2 for dioxane. In THF an increase in the fraction of the highly reactive $\sim\sim\bar{C}HPh$ ions, arising from dilution, leads to an increase in the observed k_p. The propagation constant depends on the nature of the counter ion.

At 25 ^{o}C in dioxane k_p is 0.9 for Li^{+}, 3.5 for Na^{+}, 19.8 for K^{+} and 24.5 for Cs^{+} $l\,mol^{-1}s^{-1}$. In THF the ion pair grows faster and the order of reactivity is reversed. Thus, k_p $\sim\sim^{-}CHPh, M^{+}$ is 160 for Li^{+}, 80 for Na^{+}, about 50 for K^{+} and 22 for Cs^{+}.[55] It seems that the partial solvation of the counter ion in the transition state represents a major driving force of the polymerisation in THF. Thus, a more strongly solvated M^{+} gives a more reactive ion pair, and therefore in THF the reformation of neutral species is energetically unprofitable. Hence termination mechanism does not operate in the THF either. In dioxane, the solvent apparently does not help in separating the ions in the transition state, and therefore reactivity of an ion pair is less.

In the present project, some of the objectives required the preparation of functionally terminated polystyrenes of low molecular weight. It has been reported[56] that a high initiator concentration is required in order to obtain low molecular weight polymers in any solvent by this route. In dioxane, however the initiator solubility does not permit sufficiently high concentrations to be reached. In THF, the initiation solubility was sufficiently high, so most of the polymers were prepared using this solvent.

2. PURIFICATION OF MATERIALS

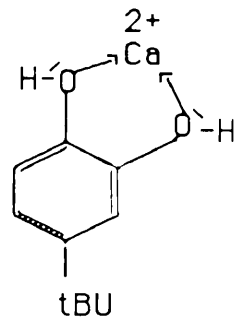
2.1. Tetrahydrofuran Manipulation

For reasons mentioned in the literature review tetrahydrofuran (THF) was used as solvent in polymerisation. THF (May and Baker) was purified by reflux over cuprous chloride and distilled over potassium hydroxide for elimination of carbon dioxide and other impurities. Immediately before use, it was poured into the apparatus as shown in Fig. 3.1. In flask A, it was refluxed over sodium metal and benzophenone. The sodium benzophenone compound was formed, then rapidly a blue colour appeared. As long as the blue colour was present this was an indication that the solution was free of impurities and it was distilled into flask B and then used immediately.

2.2. Styrene Manipulation

When selecting a purification scheme for styrene monomer, it is necessary to consider its chemical reactivity towards the drying agents.[57] For example, violent polymerisation is effected by contact with strong acids such as phosphorous pentoxide and strong bases such as lithium aluminium hydride, while rapid polymerisation occurs in the presence of sodium metal.

Styrene monomer was washed with 5% aqueous sodium hydroxide then washed with distilled water three times. It was dried over anhydrous calcium chloride during storage for 48 hours. It was then dried over finely crushed calcium sulphate. The action of calcium sulphate is two fold. Its main function is that it efficiently removes the bulk of the water in the monomer. It also reduces the volatilisable p-tert-butylcatechol inhibitor present in the monomer by complex formation as shown below;



The last stage of drying was over calcium hydride. Because of the tendency of the pure styrene to polymerise, it was finally distilled on the high vacuum line, the middle portion of the distillate being collected and then used immediately.

2.3. Dioxane Manipulation

For the purification of commercial dioxane it was refluxed with freshly cut pieces of sodium metal until the production of a yellow "slug" ceased.[58] A calcium chloride guard tube was used at top of the reflux condenser. The dioxane was then filtered and refluxed with more freshly cut sodium metal and 1g of fluorenone for one hour.

A coffee coloured mono-sodium ketyl formed. It was further refluxed for three hours, during which the solution turned a deep green due to the formation of the disodium complex and the globules of molten sodium showed a metallic lustre. The dioxane was distilled and used immediately.

2.4. Alkali Metal Handling

Sodium metal was cleaned by cutting away most of the oxide in air. The metal was then transferred to a beaker which was continuously swept out by inert nitrogen. It was then recut along all facets of the cubes. The metal thus obtained

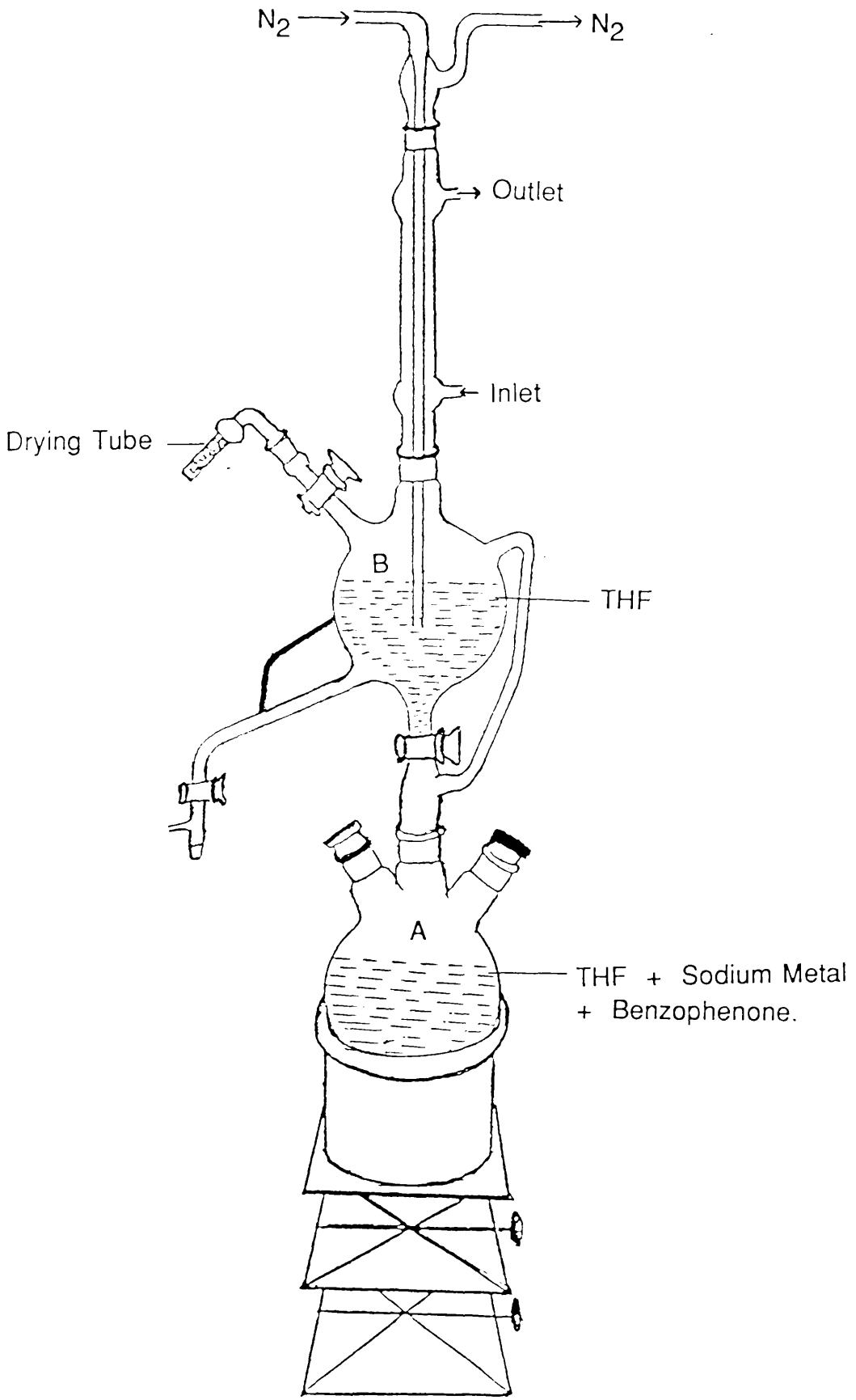


Fig. 3.1. Purification of THF.

remained reflective for at least 2 min, after cutting but then slowly lost its polish, possibly owing to surface recrystallisation. It started to react immediately when added to naphthalene suspended in a solvent.

2.5. Naphthalene Manipulation

Naphthalene was recrystallised three times from AR grade methanol, dried under vacuum at 30 ^{o}C and stored in an evacuated desiccator prior to use.

2.6. Purification of Initiator

The free radical polymerisation initiator 2,2̄-azobisiosbutyronitrile (AIBN) (Aldrich) was purified by recrystallising twice from absolute methanol, the solution being filtered hot to removed insoluble products of decomposition of the initiator.[82] The crystals were filtered off, dried under vacuum and kept in the dark at 0 ^{o}C

2.7. Purification of Styrene oxide

Styrene oxide was dried with calcium hydride and distilled under reduce pressure prior to use.

2.8. Purification of Nitrogen

The nitrogen used as inert atmosphere was obtained from British Oxygen Co. This nitrogen usually contains less than 10 ppm oxygen. It was further purified by bubbling through sulphuric acid, phosphorous pentoxide and silica gel. Nitrogen thus purified contained virtually no measurable quantity of oxygen.

2.9. Purification of Carbon dioxide

Gaseous carbon dioxide (British Oxygen Co.) was purified by passing over silica gel and phosphorous pentoxide.

Dry ice was used as supplied, without further purification, as a terminating agent. Polymerisation data has been given in Table 3.2, which shows that polymers have broad distribution due to presence of moisture in it.

3. FREE RADICAL POLYMERISATION

Polystyrene was prepared by free radical polymerisation. The reaction was carried out under vacuum and the procedure is described in detail as follows.

3.1. Introduction of Initiator into Dilatometer

A dilatometer with volume 22.5 ml was used as polymerisation vessel. The dilatometer was washed with cleaning fluid, distilled water, Analar acetone, and dried by pumping to high vacuum. It was flamed out to removed any volatile adsorbed on the glass.

The recrystallised initiator (AIBN) was introduced through a funnel into the reaction dilatometer. Any initiator sticking to the surface of the stem was washed down with Analar acetone, which was then pumped off under high vacuum.

3.2. Introduction of Monomer into Dilatometer

The dilatometer containing initiator was pumped to a pressure of 10^{-3} torr. Styrene monomer in a graduated reservoir, purified as previously described, was degassed thoroughly, then distilled at ambient temperature into the dilatometer,

the first and the last part of the distillate being rejected. Once the polymerisation mixture of the initiator and monomer had been made up in the dilatometer, it was frozen with liquid nitrogen, pumped to a pressure of less than 10^{-3} torr and then sealed.

3.3. Polymerisation

The dilatometer was warmed up to room temperature and swirled for a few minutes to dissolve initiator.

Polymerisation was carried out at 60 ^{o}C in a thermostat tank controlled to $\pm$0.1 ^{o}C. The volume contraction during polymerisation was followed to restrict conversion to around 10% for the homopolymer.

3.3.1. Polymer Isolation and Purification

After the required time, the dilatometer was removed from the thermostat and cooled. The polymer was precipitated in methanol and filtered. It was then dissolved in dichloromethane and was precipitated in methanol. The polymer was purified by three reprecipitations. Polystyrene was dried under vacuum at 40 ^{o}C and stored in an evacuated desiccator. The polymerisation data are given in Table 3.1

4. ANIONIC POLYMERISATION

In order to obtain low molecular weight polystyrene (PS) by the anionic route, it was necessary to use extremely pure solvent. Dioxane and tetrahydrofuran may be used as solvents with sodium naphthalenide initiator. It was proved by experiments that the latter was preferable, because in dioxane, the initiator can not be dissolved to give sufficiently high concentration. Data for polymers in dioxane

are illustrated in Table 3.2.

4.1. Polymerisation

The apparatus for polymerisation is shown in FIg. 3.2. It was flamed out under a stream of dry nitrogen and left for three hours. Flask (A) contained naphthalene. Pieces of sodium metal were placed in the side arm tube (B). Into this flask, THF was poured directly from the drying apparatus as shown in Fig. 3.1. The solution was stirred, sodium metal was added piece by piece at room temperature under nitrogen over six hours. The solution turned dark green due to formation of sodium naphthalenide. It was filtered through a glass sinter into a graduated cylinder (C), from which a known volume of initiator solution was passed into flask (D). The flask was equipped with a mechanical stirrer and nitrogen inlet and outlet and a graduated reservoir containing purified dry styrene was also attached. A 1 ml portion of the sodium naphthalenide solution was withdrawn and titrated against standard HCl in order to determine the initiator millequivalents. A calculated amount of styrene was then added dropwise into the vigorously stirred initiator solution. As soon as the first drop of the monomer came in contact with the initiator solution, its colour abruptly change from green to red, indicating formation of the styrene radical-anion, which is of course capable of propagation to give a chain of styrene units. To terminate the chains (as benzylic ends) a few ml of acidified methanol were added. The polymer was precipitated in acidified methanol and filtered. The polymer was dissolved in dichloromethane and the polymer solution was washed twice with 0.1M aqueous HCl to remove any sodium salt. The polymer was precipitated in methanol, redissolved in THF and precipitated in AR grade methanol. These repeated precipitation were found to be necessary in order to removed sodium salt and naphthalene effectively. The polystyrene was then dried under vacuum at 40 ^{o}C and stored under vacuum in a desiccator. The polymerisation data are given in Table 3.3.

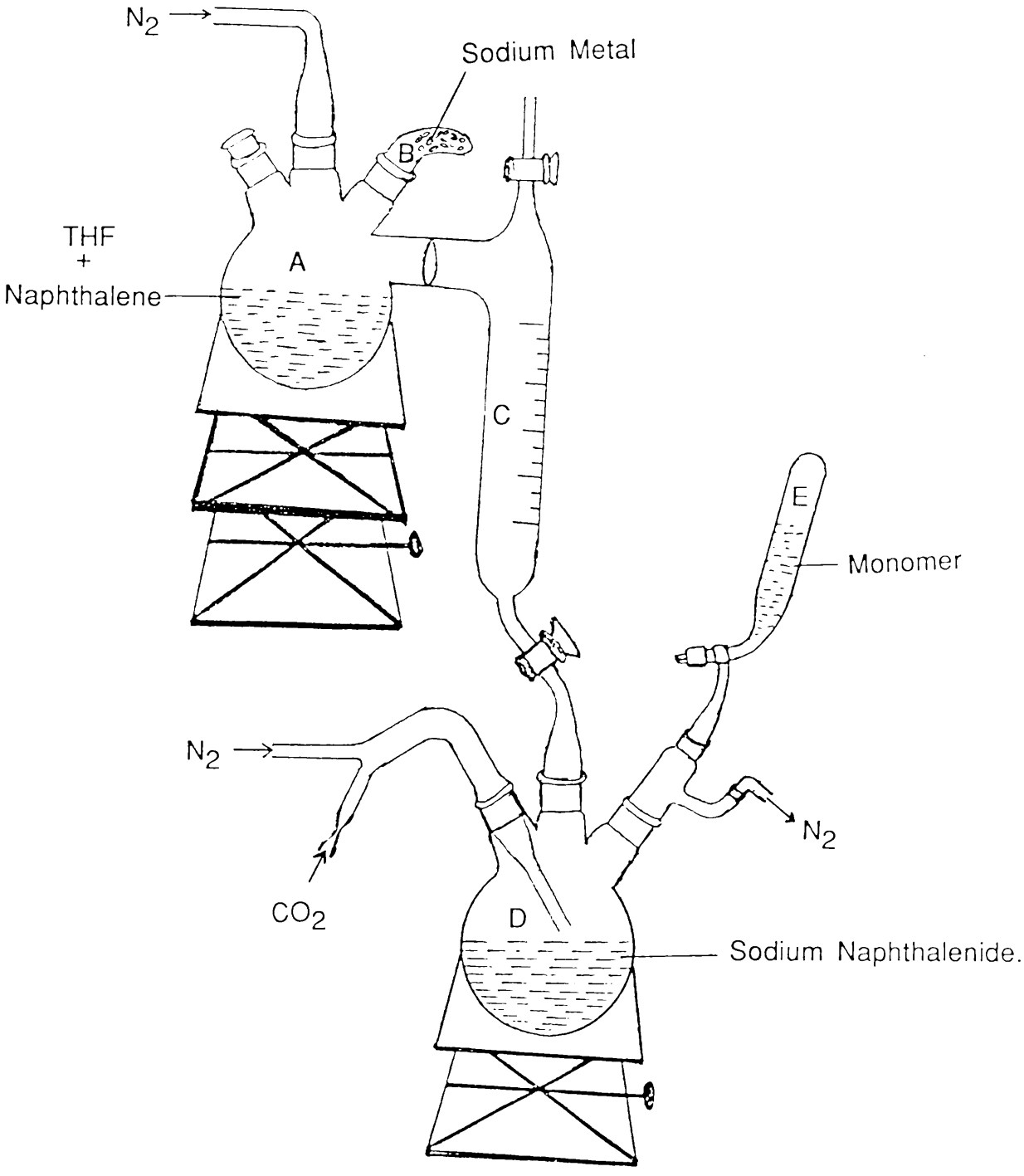


Fig. 3.2. Preparation of Polymer.

Table 3.1 Free Radical Polymerisation Data for Polystyrene.

Polymer	Amount of initiator (g)	Amount of monomer (ml)	Time hours	Weight of polymer (g)	Percentage conversion
FPS	0.01 (0.05%)	22.0	6	2.0	11.0

Table 3.2 Polymers Prepared in Dioxane

No.	Monomer (ml)	Naphthalene (g)	Sodium metal (g)	Solvent (ml)	Terminating agents	$\bar{M}n$. by GPC	Distribution	$\bar{M}w$. by viscosity
1	12.0	3.0	2.0	200	Ethylene oxide	2.9×10^4	1.82	4.1×10^4
2	15.0	3.0	2.0	300	Dry ice	1.3×10^4	1.70	2.0×10^4
3	13.0	2.5	1.5	300	Dry ice	1.2×10^4	1.9	2.0×10^4
4	20.0	3.0	2.0	300	Methanol	2.2×10^4	1.5	3.1×10^4

$\bar{M}w$ = Weight-average molecular weight

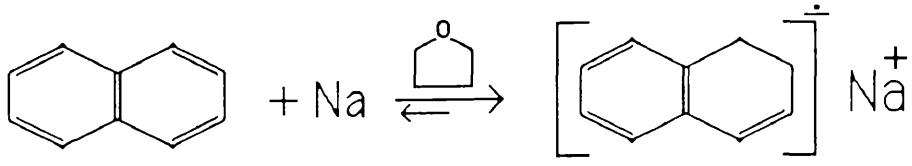
$\bar{M}n$ = Number-average molecular weight

The molecular weight of the polymer is assumed to be related to the quantities of the initiator and the monomer used by the equation.

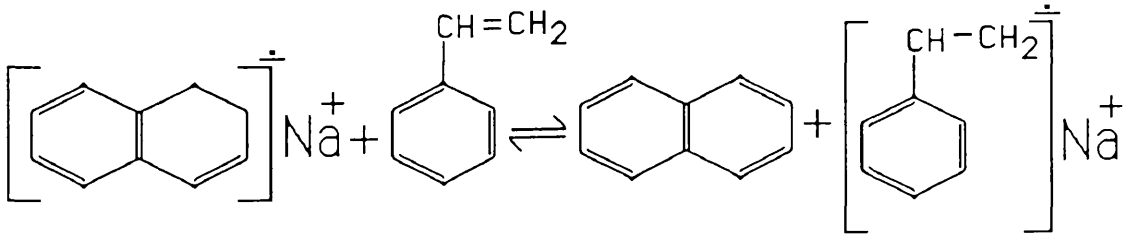
$$\bar{M}n = \text{Weight monomer (g)} / \text{Moles initiator}$$

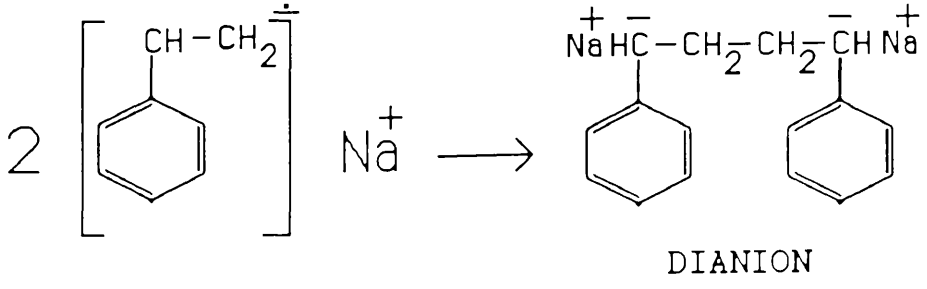
4.2. Mechanism of Polymerisation[10,68]

The formation of initiator (sodium naphthalenide) can be depicted by the following reaction;



Sodium naphthalenide reacts with styrene to form the dianion. The mechanism of formation of dianion is shown below;





DIANION

Table 3.3 Anionic Polymerisation Data for Polystyrene Prepared in THF.

Polymer	Monomer (moles)	Naphth-alene (moles)	Sodium metal (moles)	Solvent THF (ml)	Initiator (milliequivalents)
PS12	0.262	0.023	0.026	350.0	4.8
PS53	0.175	0.008	0.013	150.0	2.1
PS37	0.218	0.023	0.052	500.0	15.0

5. SYNTHESIS OF POLYMERS WITH DIFFERENT END GROUPS

5.1. Preparation of α,w-Dihydroxyl Polystyrene (HO - PS - OH)

α,w-Dihydroxyl polystyrene prepared by the polymerisation of styrene with sodium napthalenide. The red colour "living" polystyrene ion pairs were prepared by using the same method as described before. The calculated amount of styrene oxide, in a reservoir, purified as previously described, was added dropwise to the vigorously stirred solution. To terminate the chains (as α,w-dihydroxyl ends), a few ml of acidified methanol were then added. The polymer was then precipitated and purified as described previously.

5.2. Preparation of α,w-Dicarboxylic Polystyrene (HO_2C-PS-CO_2H)

Extremely dry carbon dioxide was passed through the living polystyryl solution by using the apparatus, shown in Fig. 3.2. The red colour disappeared instantaneously and a viscous fluid was obtained due to the formation of dicarboxyl ions. A few ml of acidified methanol were added. The polymer was then precipitated and purified. Data for polymers are given in Table 3.4.

5.2.1. Preparation of Disodium Salt from Diacid Terminated Polystyrene

An approximately 0.1M solution of sodium hydroxide was prepared in methanol (AR). Acid terminated-polystyrene was dissolved in THF. This solution was neutralised with freshly prepared sodium solution, using phenolphthalein as indicator, then added to methanol. The white precipitate of the sodium salt of polystyrene was filtered, dried under vacuum and stored in a desiccator. The IR spectrum of the polymer is given on page 64.

5.2.2. Preparation of Calcium Salt of Dicarboxyl-Terminated Polystyrene

The synthesis of the calcium carboxylate salt of polystyrene was attempted by the following methods.

5.2.2.1. Stoichiometry

The stoichiometric amount of dicarboxyl-terminated polystyrene (THF solution) was mixed and stirred with calcium chloride (in methanol) and refluxed for 12 hours.

5.2.2.2. Melt Polymerisation

Dicarboxyl-terminated polystyrene (HO_2C-PS-CO_2H) and calcium chloride were heated at 180 ^oC, with constant stirring for six hours under a slow stream of nitrogen.

5.2.2.3. Interfacial Polymerisation

Polymer (HO_2C-PS-CO_2H) was dissolved in dichloromethane. 5% aqueous solutions of sodium lauryl sulphate and calcium chloride were prepared. First calcium chloride was mixed with sodium lauryl sulphate solution. The polymer solution was then mixed with this solution and the mixture was stirred for an hour. The polymer solution was separated and the polymer was precipitated in Analar methanol.

5.2.2.4. Metal Exchange Polymerisation

Polymer (NaO_2C-PS-CO_2Na) was dissolved in THF and a saturated solution of calcium chloride was added. The mixture was stirred for one hour. The polymer

Table 3.4 Polymerisation Data for HO-PS-OH and HO_2C-PS-CO_2H

Polymer	Sodium metal (moles)	Naphth-alene (moles)	Styrene (moles)	THF (ml)	Initiator (millieq-uivalents)	Termin-ating agents
HO-PS-OH	0.065	0.023	0.175	500	18.5	Styrene oxide
HO_2C-PS-CO_2H	0.065	0.027	0.175	600	20.1	CO_2
HO_2C-PS-CO_2H	0.052	0.019	0.218	500	15.5	CO_2
HO_2C-PS-CO_2H	0.043	0.015	0.262	500	11.5	CO_2

was then precipitated in Analar methanol.

None of the above methods were successful in giving the calcium salt. Finally, the following approach was utilised.

Dicarboxyl-terminated polystyrene (Sample *, Table 3.4) was dissolved in THF and an excess of calcium hydroxide was added. The mixture was then refluxed for three hours. Calcium hydroxide in excess was filtered and the filtrate was poured into methanol.The white precipitate of the calcium salt of polystyrene was filtered and dried under vacuum and stored in a desiccator. The IR spectrum of calcium salt of polystyrene is given on page.64.

5.2.3. Preparation of Zn Salt of Dicarboxyl-Terminated Polystyrene

A THF solution of dicarboxyl-terminated polystyrene (HO_2C-PS-CO_2H) ($\bar{M}n$ 2334) was refluxed with zinc powder for two hours. The polymer was then precipitated, dried under vacuum and stored into a desiccator. The IR spectrum of the zinc salt of polystyrene is given on page 64.

5.2.4. Preparation of Diacid chloride-Terminated Polystyrene (ClOC-PS-COCl)

The replacement of the hydroxyl group of carboxyl-terminated polystyrene with chlorine was followed by previously reported methods.[59,60] The dicarboxyl-terminated polystyrene ($\bar{M}n$ 2334) was dissolved in toluene, and phosphorous pentachloride was added to it. The mixture was stirred at ice temperature for a few minutes under nitrogen and then at room temperature for 24 hours. The resulting solution was poured into n-hexane and the polymer was filtered and dried under vacuum at 30 ^{o}C. For the present studies, this method was not useful. This may be due to the presence of moisture as phosphorous

pentachloride itself is moisture sensitive. Another method was therefore used for the preparation of diacid chloride-terminated polystyrene which is also reported in the literature.[61-63]

A dilute (5%) toluene solution of dicarboxyl-terminated polystyrene was placed in a 100 ml round bottomed flask. Then 30 equivalents of freshly distilled thionyl chloride was added into the solution. The solution was refluxed for 12 hours. The unreacted thionyl chloride and solvent were evaporated under vacuum. The polymer was stored in a desiccator under vacuum.

6. CHARACTERISATION

Polymers were characterised by elemental analysis, gel permeation chromatography, viscometry, end group analysis, infrared spectroscopy and nuclear magnetic resonance spectrometry.

6.1. Molecular Weight Measurements[166]

Molecular weights of polymers were measured by gel permeation chromatography (GPC), viscometry and end group analysis.

6.1.1. Gel Permeation Chromatography[69,70]

Gel permeation chromatography provided as a service from Polymer Supply & Characterisation Centre was employed for determining the number average molecular weight ($\bar{M}n$). The results are summarised in Table 3.5.

6.1.2. Viscometry

The intrinsic viscosity [η] (dl/g) of the polymers was obtained by dilute solution viscometry at 25 ^{o}C in toluene.[44,46]

A correlation of intrinsic viscosity with molecular weight for linear polymers can be achieved through the empirical equation proposed by Mark and Houwink,[44,56,71] based on earlier work by Staudinger.[72]

$$[\eta] = KM^{\alpha}$$

Where M is molecular weight, and K and are constants for a particular polymer-solution system. Viscometric molecular weight determination has been extensively reviewed[73-75] and K and α values for polymer-toluene have been taken from the Polymer HandBook.[164]

6.1.3. End Group Analysis

Functional end group content can be determined by chemical, radiochemical and physical methods.[119] The choice depends largely on the sensitivity of the method and hence the range of molecular weights which can be determined.

End group determinations are applicable and useful for molecular weight less than 25,000.[119] This approach gives a number-average value and depends on the polymer having a terminal group, or groups, on each chain which can be quantitatively measured. When there are no losses of end groups by side reaction, no production of additional end groups by branching, and when all ends can be accurately determined, a direct measure of the number-average molecular weight can be made.[76,77]

In the present studies, hydroxyl equivalent for the dihydroxyl-terminated polystyrene, has been determined as described by Subhas and co-workers.[78,79]

The molecular weight of the diacid-terminated polystyrene has been obtained from the acid number. A solution of the polymer in THF was titrated with

0.125M KOH in methanol. The acid number determined by the use of the formula below.;

$$\text{Acid Number} = (B-A)M \times 56.1/W$$

B = ml of KOH required for blank titration.
A = ml of KOH required for polymer solution titration.
M = molarity of the KOH solution.
W = grams of polymer used.

The molecular weight data for polymers are given in Table 3.5

6.2. C,H Analysis

The percentage of carbon and hydrogen were obtained from microanalysis and the percentage of oxygen was calculated by difference. The results are listed in Table 3.6.

6.3. Metal Contents[43,65]

Sodium was analysed by flame photometry and calcium and zinc were analysed by atomic absorption spectroscopy. The details of the methods employed are given below;

6.3.1. Determination of Sodium, Calcium and Zinc

Atomic Spectroscopy

This approach is based upon the absorption, emission, or fluorescence of electromagnetic radiation by atomic particles. It is divided into three types, (a)

Table 3.5 Molecular Weight Data of Polymers

Polymers	$\bar{M}n$ by GPC	$\bar{M}w/\bar{M}n$	$\bar{M}w$ by viscos-ity	$\bar{M}n$ end group analysis
PS12	12,000	1.4	15,000	----
PS53	53,000	1.30	58,000	----
PS37	3,740	1.20	5,000	---
PS180	180,000	1.70	189,000	---
HO-PS-OH	6,228	1.5		7,200
HO_2C-PS-CO_2H	2,334	1.30	5,000	3,200
*				
ClOC-PS-COCl	2,500	1.32	---	---
HO_2C-PS-CO_2H	5,532	1.60	6,000	8,500
*				
NaO_2C-PS-CO_2Na	2,450	1.30	---	
*				
~O_2C-PS-CO_2-Ca~	5,970	1.7	---	
*				
~O_2C-PS-CO_2-Zn~	4,872	1.60	---	

*

Made from HO_2C-PS-CO_2H ($\bar{M}n$ = 2,334)

Table 3.6 Microanalysis Results

Polymers	Calculated			Observed		
	%C	%H	%O	%C	%H	%O
PS12	92.31	7.69	Nil	92.33	7.67	Nil
PS53	92.31	7.69	Nil	92.40	7.60	Nil
PS37	92.31	7.69	Nil	92.44	7.60	Nil
HO-PS-OH	91.78	7.69	0.51	91.60	7.76	0.64
HO_2C-PS-CO_2H (Mn 2334) *	89.71	7.56	2.71	90.71	7.84	1.43
ClOC-PS-COCl	88.61	7.36	1.28	88.89	7.25	1.28
HO_2C-PS-CO_2H (Mn 5532) *	90.72	7.56	1.71	90.22	7.89	1.89
NaO_2C-PS-CO_2Na *	89.29	7.15	1.38	87.13	7.66	3.03
~O_2C-PS-CO_2-Ca~ *	88.79	7.39	2.74	87.45	7.87	3.56
~O_2C-PS-CO_2-Zn~	88.61	7.73	2.61	86.23	7.36	5.19

*

Made from HO_2C-PS-CO_2H ($\bar{M}n$ 2334)

atomic emission, or flame photometry, (b) atomic absorption, and (c) atomic fluorescence.[43]

Polymer samples containing metal ions were accurately weighed into porcelain evaporating dishes and heated in an oven at 600 ^{o}C to destroy the organic part of the sample and convert them into the corresponding oxides. A few ml of concentrated HNO_3 were added to the same dishes which were then placed on a steam bath until brown fumes ceased to be evolved. The solution so obtained was transferred into a volumetric flask with washings and made up to 100 ml with deionised water. Solutions of known concentration of Na^+, Ca^{++} and Zn^{++} from their nitrates [$NaNO_3$, $Ca(NO_3)_2$, $Zn(NO_3)_2$] were made as 1.0, 0.8, 0.4 and 0.2 parts per million. Solutions of these were sprayed and readings were taken.

Calibration curves were prepared by plotting these readings against the concentrations giving a straight line in each case. The concentration of the unknown solution for analysis could then be found using flame photometer and atomic absorption spectrophotometer. By comparing the readings with the calibration curves, the percentage of sodium, calcium and zinc could be calculated. The results are shown in Table 3.7.

6.4. Proton Magnetic Resonance Spectrometry

A simple way of characterising polystyrene and functionally terminated polystyrene is by proton NMR spectrometry. Figs. 3.3 and 3.4 (a,b) illustrate the ability of this approach to separate the proton signals due to the aromatic polystyrene chain from those of the hydroxyl proton and carboxyl proton.

In the case of polystyrene in Fig. 3.3, there is a singlet at 1.5∂ which is associated with methylene (-CH_2-) protons. A broad singlet at 1.8∂ is due to the

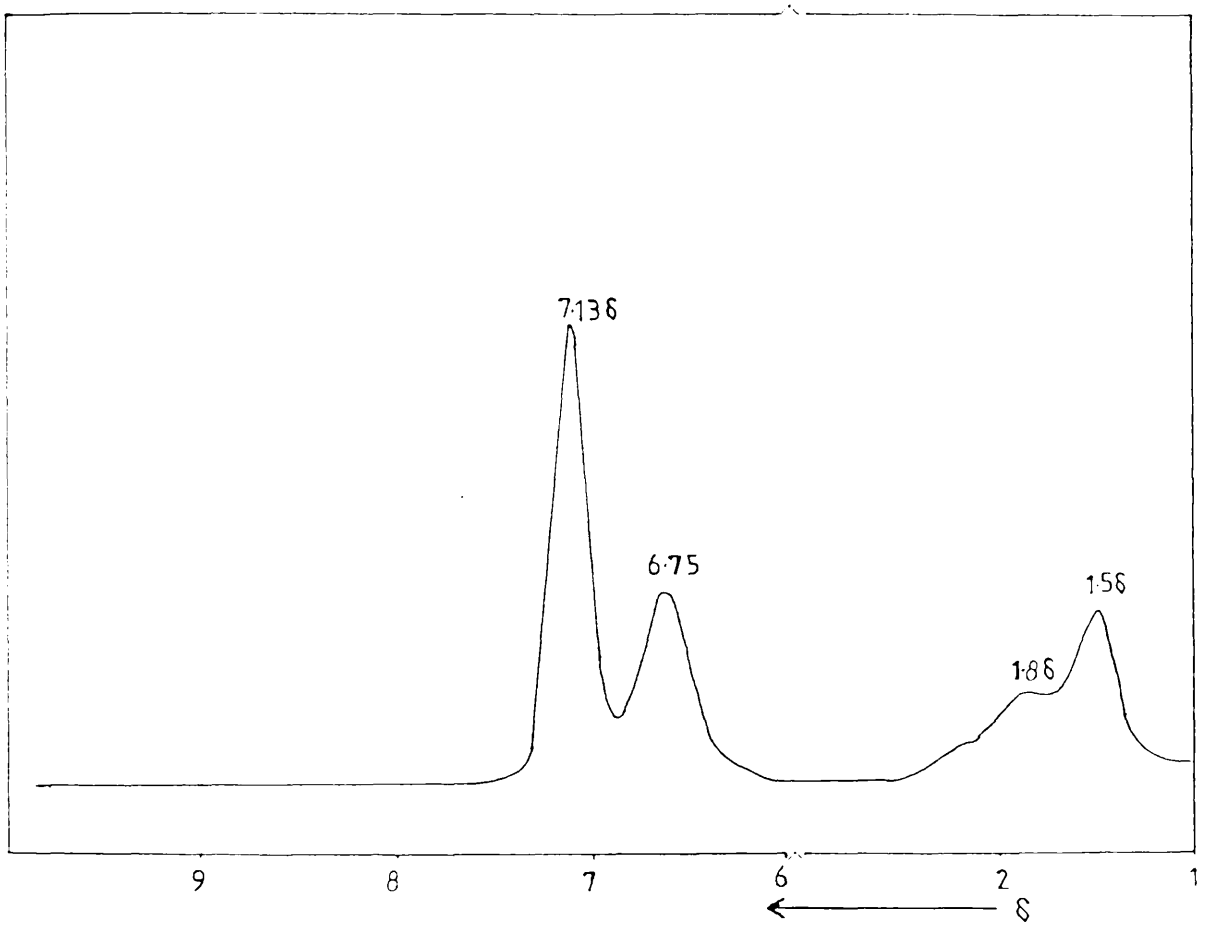


Fig. 3.3. NMR spectrum of Polystyrene.

Keys: 1.5δ; $-CH_2-$, 1.8δ; -CH-, 6.75δ; o-Aromatic Proton, 7.13δ; m,p-Aromatic Proton.

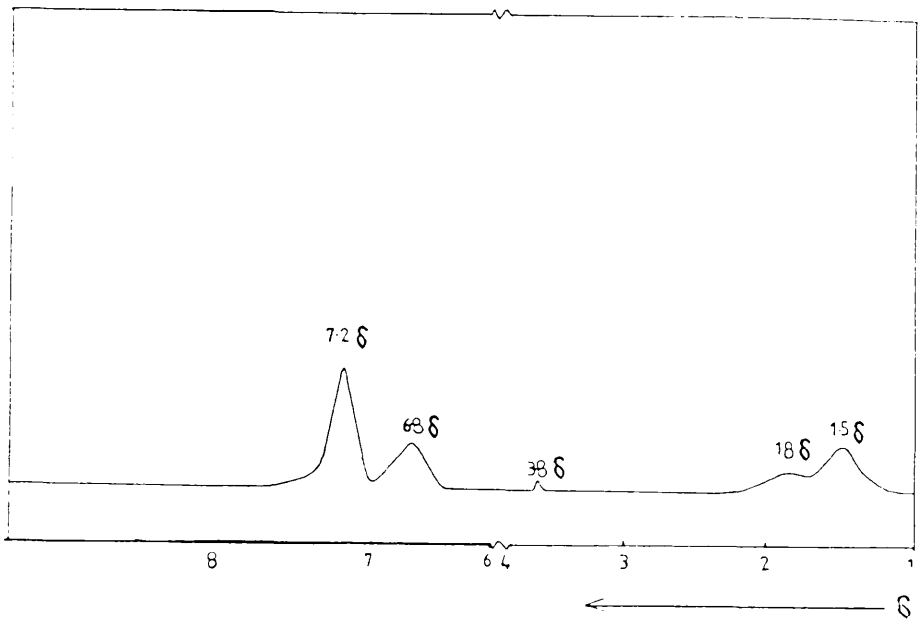


Fig. 3.4a. NMR spectrum of HO-PS-OH.

Keys: 1.5δ; $-CH_2-$, 1.8δ; $-\underset{|}{C}H-$, 6.7δ; o-Aromatic Proton, 7.2δ; m,p-Aromatic Proton, 3.7δ, Hydroxyl Proton.

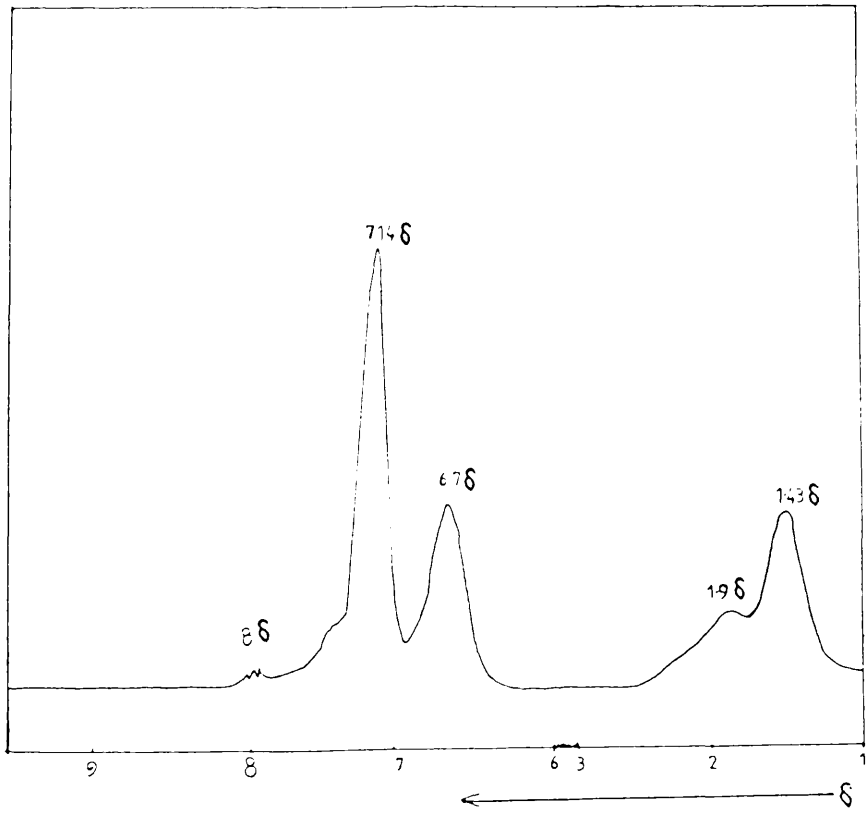


Fig. 3.4b. NMR spectrum of HO_2C-PS-CO_2H.

Keys: 1.43δ; $-CH_2-$, 1.9 ; $-\underset{|}{C}H-$, 6.7δ; o-Aromatic Proton, 7.14δ; m,p-Aromatic Proton, 8.0δ; Acidic Proton.

Table 3.7 Atomic Spectroscopic Data for Na, Ca and Zn Polymers

Polymer	%Metal Calculated	%Metal Observed
NaO_2C-PS-CO_2Na	1.43	1.87
~O_2C-PS-CO_2-Ca~	1.07	1.12
~O_2C-PS-CO_2-Zn~	1.05	1.20

methine proton (-CH-). There are two signals for aromatic protons, one at 6.75∂ due to ortho situated protons and the other at 7.13∂ due to meta and para protons.

The ^1H NMR spectra of anionic and free radical polystyrene are similar. These spectra are very close to that reported for polystyrene by Inove and co-workers [80] at 110 MHZ with the same solvent. These are also very close to that given by Malhotra et al,.[81] They also found no difference between anionic and free radical polystyrene spectra.

The hydroxyl-terminated polystyrene, Fig. 3.4 (a) has one extra singlet at 3.78∂ due to hydroxyl protons (-CH_2-OH). For carboxyl-terminated polystyrene, in Fig. 3.4 (b), there is a cluster of signals at 8.0∂ due to the acidic proton. The rest of the signals are the same as in the polystyrene specrtum.

6.5. Infrared Spectroscopy

The IR spectra were obtained by the KBr technique using 1-2 mg of sample and 200-300 mg of KBr. The polystyrene spectrum complete with peak assignment is given in Fig. 3.5.

The IR spectrum of styrene differs from that of the homopolymer in the appearance of extra bands at 990, 910, 1410, 1625 cm^{-1} which are due to C-H wag of vinyl group (-C = C-H), C-H deformation (-C = C-H) and C = C stretching, respectively.

Fig. 3.6 (a,b,c) shows IR spectra of dihydroxyl, dicarboxyl and diacid chloride-terminated polystyrene, respectively. Fig. 3.6 (a) shows a band at 3450-3200 cm^{-1}, which is characteristic of -OH absorption. In Fig. 3.6 (b), there is a sharp peak at 1700 cm^{-1} due to C = O absorption. There is also bands at 2700-2400 cm^{-1} which is characteristic of the strongly H-bonded O-H of a carboxylic acid. Fig. 3.6 (c) shows a band at 1790 cm^{-1} due to O = C - Cl absorption. The remaining peaks in all these spectra are the same as in the polystyrene spectrum. IR spectra for metal salts of dicarboxyl-terminated polystyrene are shown in Fig. 3.7(a,b,c). The C=O stretching frequency in dicarboxyl-terminated polystyrene is at 1700 cm^{-1} but in the case of the salts the C=O frequency is shifted to lower wave numbers by 140 cm^{-1}. In the case of divalent metal salts, the C=O absorption is broader as compared to the monvalent salt. The rest of the spectra are similar to polystyrene. Previously McNeill and Zulfiqar[66] also observed the similar differences in the IR spectra of metal carboxylate side groups in salts of poly(methyacrylic acid).

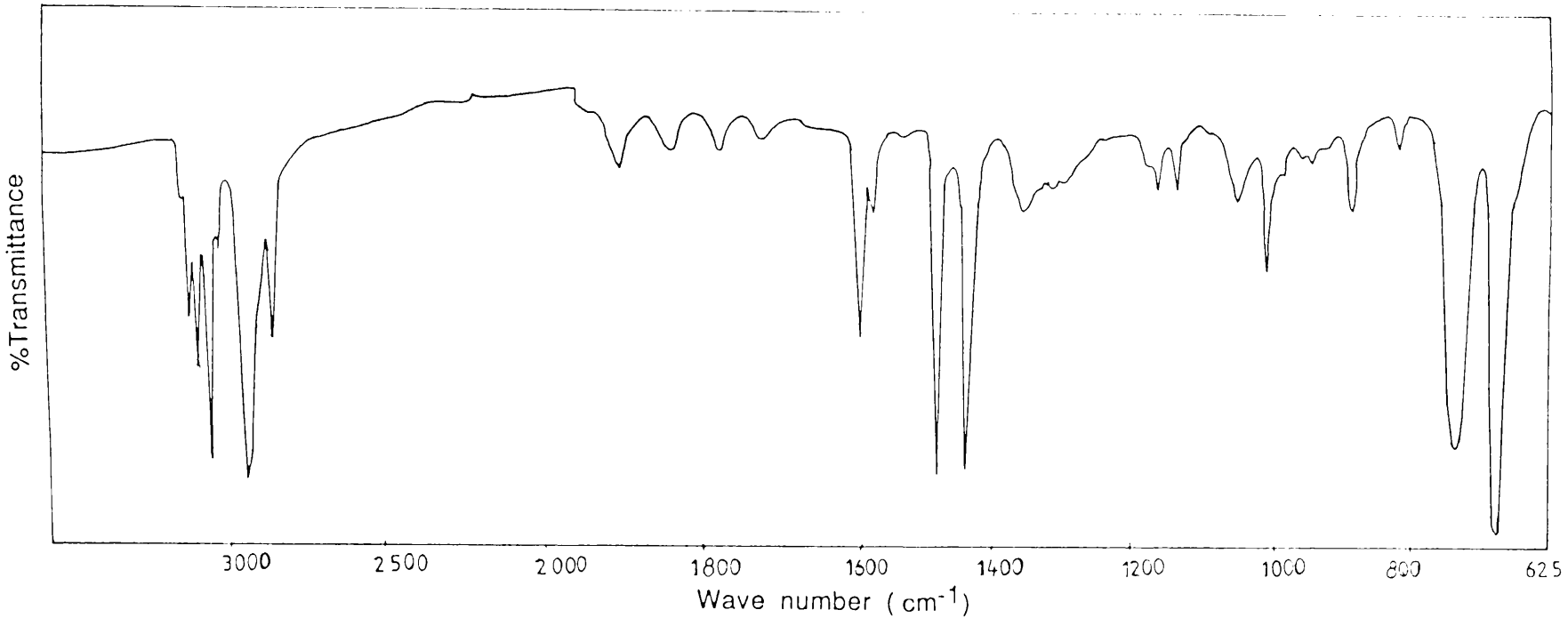


Fig. 3.5. Infrared spectrum of Polystyrene.

Keys:		
	3080, 3060, 3020 (cm^{-1})	Aromatic C-H stretch
	2920,2820 (cm^{-1})	Saturated C-H stretch
	2000 – 1800 (cm^{-1})	Monosubstituted aromatic ring patterns
	1600, 1590 (cm^{-1})	Aromatic C-H ring vibration
	750, 690 (cm^{-1})	Out of plane C-H ring vibration

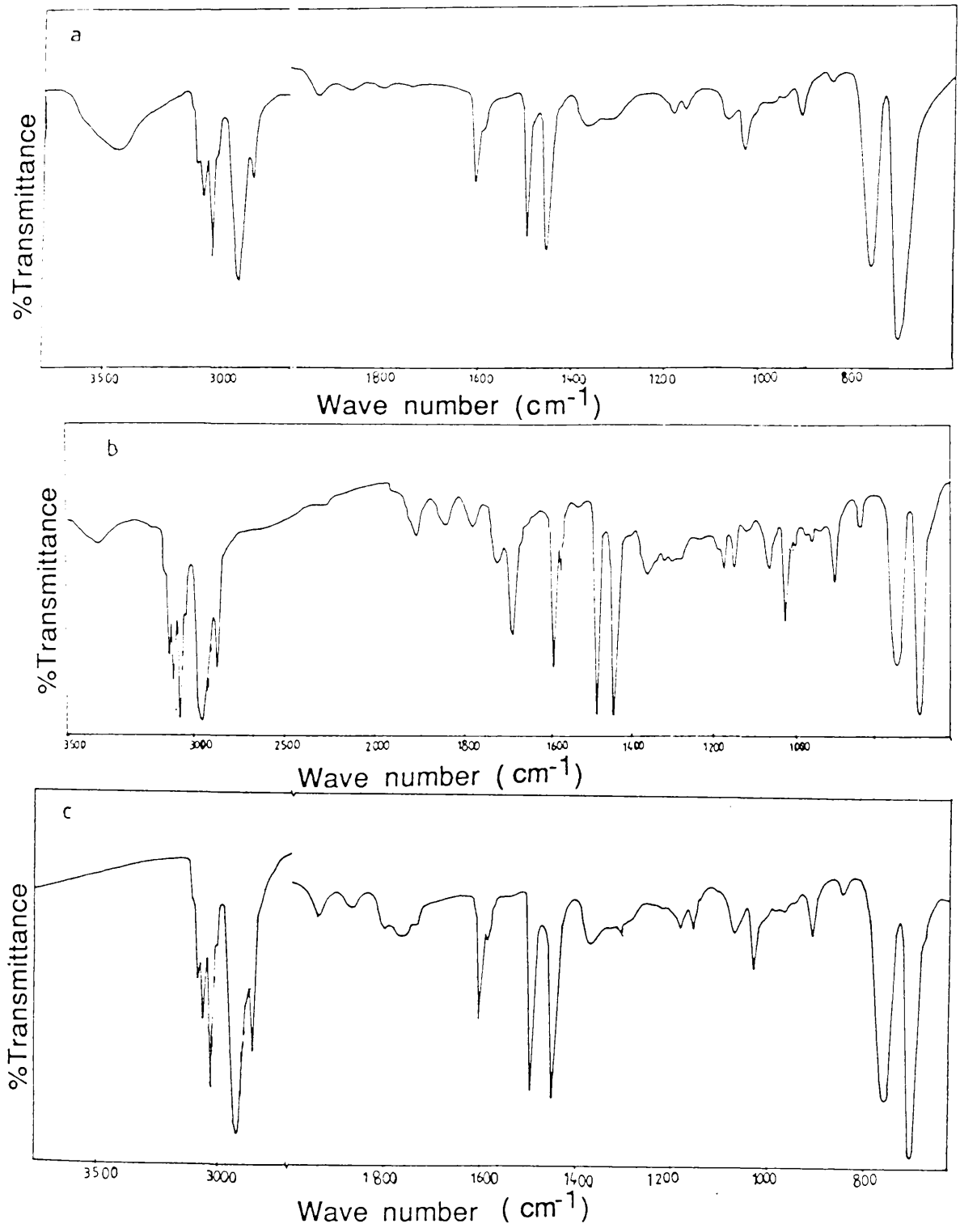


Fig. 3.6. Infrared spectra of functionally terminated Polystyrenes.
(a) Dihydroxyl (b) Dicarboxylic acid (c) Diacid chloride

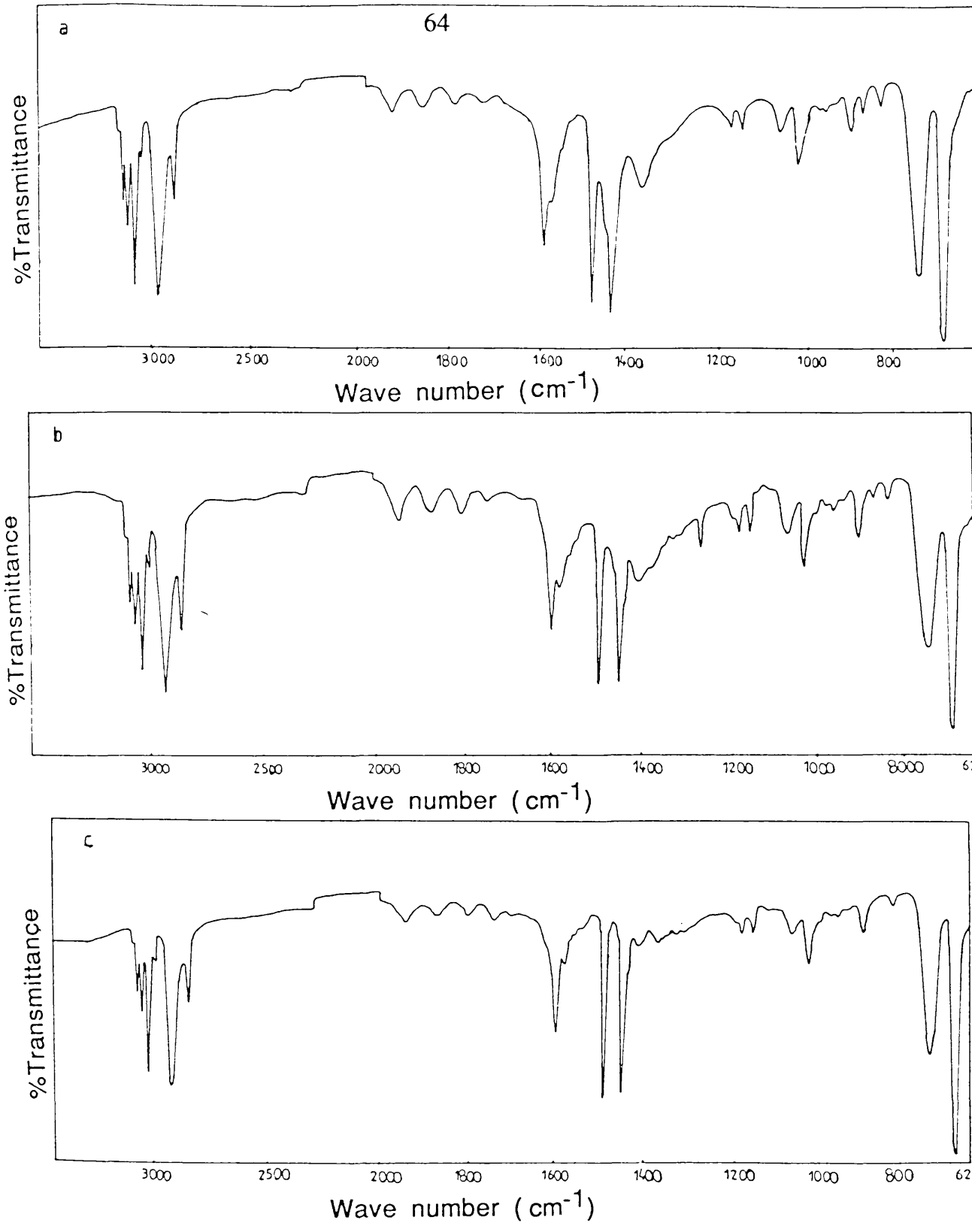


Fig. 3.7. Infrared spectra of salts of dicarboxyl-terminated Polystyrene.

Keys: (a) Na (b) Ca (c) Zn

CHAPTER FOUR

THERMAL DEGRADATION OF POLYSTYRENE

1. INTRODUCTION

Polystyrene is relatively inert chemically and relatively non-polar, having a dielectric constant of 2.50 and 2.56 (10 KHZ at 25 ^{o}C) for anionic and radically prepared samples, respectively.[120,123] It is quite resistant to strong alkalis, halide acids, and oxidizing and reducing agents, but is readily attacked by a large variety of solvents.[121,122]

Polystyrene is cheap, easily fabricated and possess excellent insulating properties. Its high refractive index (1.6) makes it useful for plastic optical components. Alkylated polystyrenes have been used as oil additives.[124] Many polystyrene based materials are used in the building industry and for the production of furniture, car parts[125] etc.

2. LITERATURE REVIEW OF THERMAL DEGRADATION OF POLYSTYRENE

The thermal decomposition of polystyrene has been the subject of considerable interest for many years. The first systematic study of polystyrene degradation was attempted by Staudinger and Steinhofer.[126]

These authors cracked polystyrene in vacuo and in air and distilled the products. The products they obtained convinced them of the head to tail addition nature of polystyrene. Later on Midgley and co-workers[127] and Whitby[128] also carried

out experiments on the destructive distillation of polystyrene.

Jellinek[129] studied the thermal degradation of polystyrene in vacuo at about 300°C. The results showed several discrepancies from the theory developed by Simha and Mark.[130] Later Jellinek pyrolysed[131] polystyrene to differing extents of degradation and obtained a molecular weight versus extent of degradation curve. This coupled with the large quantities of monomer produced in the process convinced him that monomer was being formed not as a product fraction of a random scission process but by an unzipping process initiated at active sites formed upon random weak link scission in the material. He gave a more detailed elucidation of the formation of monomer and extended the investigations to higher temperatures, at which this reaction is predominant.[132] Atherton[133] repeated Jellinek's work on polystyrene, heating the 20 mg polymer sample in a crucible, and found that a good deal of splattering occurred during the heating of the samples.

Madorsky and co-workers[134,135] were perfecting the isothermal TG technique as applied to polymer thermolysis. The rate of polymer volatilisation was found to reach a maximum at 30-40% weight loss. This was assumed to be consistent with an end-unzipping process, with some random degradation taking place simultaneously.[135]

Knight[114] used pyrolysis-gas chromatography for elucidation of the mechanism of thermal degradation. He found styrene as a major product in yields from 40 to 100%. The major experimental differences were sample size and pyrolysis temperature.

Bradt and co-workers[136] attempted a volatile product analysis for polystyrene degradation using mass spectrometry. The composition of the volatile and cold ring product fractions taken together was found to be independent of conversion.

This further discredited the random scission theory of degradation and suggested that intramolecular transfer may play a major role in the degradation process.

Grassie and co-workers[108,137-140] further investigated the characteristics of polystyrene degradation, concentrating especially upon the early stages of degradation. They observed[108] that the absolute rate of the reaction in the temperature range 280°-300 °C as well as the acceleration in rate are small. They showed that conversion against time curves are always quite smooth to high conversions and therefore contradict Jellinek's proposition that the "weak link" scission phase and the later stage of the reaction are separable experimentally.

Simha and others[141-143] and Brown[144] on the other hand, maintained that there was no essential difference between the earlier and later stages of the degradation of the polystyrene and that the decrease in molecular weight was entirely due to intermolecular transfer. Simha and Wall[145,146] made a more detailed comparison of calculated and observed changes in molecular weight.

An investigation was made [137] to associate weak links with one or more of the polymerisation variables. In fact, the weak links concentration was found to be dependent only upon the temperature of the polymerisation. Some possible structures were discussed and examined.

Cameron and Grassie[140] obtained high head to head concentrations in polystyrene by copolymerising with trace quantities of stilbene. The copolymers so produced did not posses any marked instability at small percentage conversions. The weak link content estimated by the initial molecular weight drop in the early stages of thermolysis, however, was found to approximate to that of main chain unsaturation as measured by ozonolysis. Main chain unsaturation increases with the temperature of polymerisation. For these reasons weak links were initially associated with main chain unsaturation.

The most plausible alternative approach to the system under discussion was developed by Madorsky and co-workers,[110,147,125] who asserted that the initial precipitous molecular weight drop in the system was caused by intermolecular transfer, which produced random scission in the polymer backbone. They supported Grassie's view that depropagation was an end initiated process. They made no distinction, however, between the processes operating in the initial and final stages of degradation. The gentle molecular weight drop observed in the latter stages of degradation was explained by postulating long kinetic zip lengths of depropagation.

A computer program was compiled by Wall and co-workers[147] based upon the kinetic scheme assumed to be operative within the degrading polymer. The simulated volatilisation curves so produced, approximated best to those of the real system when a large value of ∂ (the intermolecular chain transfer constant) and a small value of μ (the ratio of the random to end initiation rate constants) was used.

The kinetic approach of Madorsky group was based on the assumption that the termination process in the degradation is second order. This was in opposition to the Grassie approach which assumed first order termination. The effect of the order of the termination process upon the molecular weight distribution of the material was discussed[147] with special reference to the degradation of monodisperse anionic polymers. If termination is first order and brought about by a process of small radical ejection from the system, then a most probable molecular weight distribution should be rapidly achieved with initially monodisperse polymers. This was not found to be the case. This evidence was taken as supporting the predominance of second order termination. Of interest was the complete absence of volatilisation in the early stages of degradation of these polymers. This effect cannot be satisfactorily explained using a kinetic scheme which does not take into account the existance of a small concentration of

thermolabile bonds in the polymer molecules.

The thermal behaviour of anionic polystyrene was investigated by Rudin, Samanta and Reilly.[148] Kinetic data were obtained which suggested that degradation of polystyrene is generally zero order for about the 25% of the reaction and first order thereafter.

Richards and Salter[149] have established the importance of an intermolecular chain transfer reaction in the thermal degradation of polystyrene by a radiochemical method. Labelled, anionic polystyrene was found to be more stable than radical polystyrene with respect to emission of volatilies, at the abnormally low temperatures used in these studies.

McNeill and co-workers[150,151] also measured main chain unsaturation by tracer methods. Their degradation results did not associate weak links with unsaturation.

The weak link theory was declared unsound by Cameron and Kerr[154] because the weak link concentration in the sample (ß) apparently varied with the temperature of degradation. A simple, elegant, kinetic treatment[155] emphasised that first order termination is the predominant process in polystyrene degradation. The proposed mechanism of termination by small radical ejection from the sample was, however, proved invalid by a consideration of its effect on the molecular weight distribution of the sample.[117] The proposal made that random scission in the polymer backbone is immediately accompanied by a process of disproportionation, however, remains valid.

Cameron and co-workers[152,153] drew these observations into the following kinetic scheme. Initial scissions in radical polymers occur at weak linkages of unknown composition in the material. Degradation immediately afterwards is

initiated at abnormal linkages such as main chain unsaturations and head to head groupings. Afterwards and until the end of the degradation, initiation is at unsaturated chain ends formed by the immediate disproportionation reactions which follow normal random scissions. Termination is a first order process. A plausible (though unsubstantiated) mechanism was proposed.

Cameron and McWalter[156] studied the role of transfer reaction in the thermal decomposition of polystyrene. The model of investigation, in which they assumed no intramolecular transfer occurred and the weight composition of the volatile material and the RMM (relative molar mass) of the volatile oligomers was computed. It was also assumed that the latter are produced predominately by intermolecular transfer following radical formation at chain ends. They concluded that this model is inadequate and that it is necessary to include intramolecular transfer in the overall mechanism.

Chiantore et al.[157] isolated the first step in the thermal degradation of polystyrene prepared by radical polymerisation by heating the polymer in the temperature range 199°-280 °C. Isothermal heating of a polystyrene sample for two hours at 200°-280 °C caused a slight decrease in the molecular weight of the polymer. As the temperature is increased to 210 °C, the molecular weight progressively decreases to a value that depends on the original molecular weight of the sample, and then remains constant up to about 280 °C. Above this temperature, the molecular weight decreases very rapidly, as on the basis of the well established behaviour of polystyrene. These workers have shown that the fall in molecular weight as a function of time indicates random scission of the backbone. Costa and co-workers[158] have also observed that a similar plot for polystyrene prepared by anionic polymerisation supports the view that there is additional chain scission due to weak links.[152]

Sato et al.[159] studied the thermal degradation of polystyrene in various kinds of

solvents. They observed that the conversion of polystyrene to low molecular weight products was affected by the hydrogen donating ability of a solvent.

The mechanism of bulk thermal degradation of polystyrene was studied by Cameron et al. [160] and it was concluded that chain scission occurred by at least three concurrent processes of markedly differing rates; rapid "weak link" scission, slow normal bond scission and scission at an intermediate rate.

Although many studies have been devoted to the understanding of the mechanism of the thermal degradation of polystyrene, many questions remain unanswered. Interest continues for both practical and fundamental reasons. It seem to safe to conclude that the production of volatile products is caused chiefly by reaction involving benzylic ($\sim CH_2$-$\dot{C}HPh$) radicals, and that the termination mechanism is a first order process, at least when the temperature is lower than 350 ^{o}C.

One aspect of critical importance in relation to any explanation of the observed behaviour of polystyrene is the zip length for depropagation and intramolecular transfer. In early studies, this was believed to be very short, possibly four units or less, but Guaita [105] has concluded from computer simulation studies that the zip length is about 50 units. This value is more consistent with the levelling of molecular weight at about 5,000, discussed by Ide et al., [118] since chains initiated by end or random scission initiation at this molecular weight level should disappear completely.

3. AIM OF THIS WORK

In the present work, the programmed thermal degradation of anionic and free radical polystyrenes has been investigated using TVA, TG and DTA techniques to provide a basis for a series of studies of the degradation of modified polystyrene samples (functionally terminated, metal salts of dicarboxyl-terminated polystyrene

and linked block polystyrene) using the same experimental approach. The condensable volatile liquid products from the TVA degradation to 500 ^{o}C were separated by the SATVA method.

4. PROGRAMMED THERMAL DEGRADATION

The thermal behaviour of two polystyrene samples[anionic (PS37) and free radical (PS180)] has been investigated using TVA, DTA, TG and DTG techniques. The polystyrene samples were prepared as described in Chapter Three.

4.1. THERMAL VOLATILISATION ANALYSIS

The polymers were examined as 60 mg powder samples in a TVA system under vacuum as described in Chapter Two. Programmed heating was at a rate of 10^{o}C/min. The TVA curves for both polymers are shown in Fig. 4.1 (a,b).

It is clear from the TVA traces of PS37 and PS180 that in each case decomposition begins above 310 ^{o}C, but appreciable rates of breakdown are observed only at 320^{o} and 350 ^{o}C, respectively. Both homopolymer samples show single stage decomposition and from inspection of the separation of the traces, it is evident that products composition is same in each TVA curve, the product volatility becoming greater as the degradation temperature rises.

In both cases, the 0^{o} and -45 ^{o}C traces are separated and rest of the traces (-75^{o}, -100^{o} and -196 ^{o}C) remain with the base line. This indicates that there is no formation of non-condensable products and very volatile condensable products. The volatile liquid products are produced during the degradation of homopolymer samples to 500 ^{o}C under normal TVA conditions. In both cases the "limiting rate" effect observed in the -45 ^{o}C curve indicates that condensable volatile material is being produced which is retained by this trap but shows a significant vapour

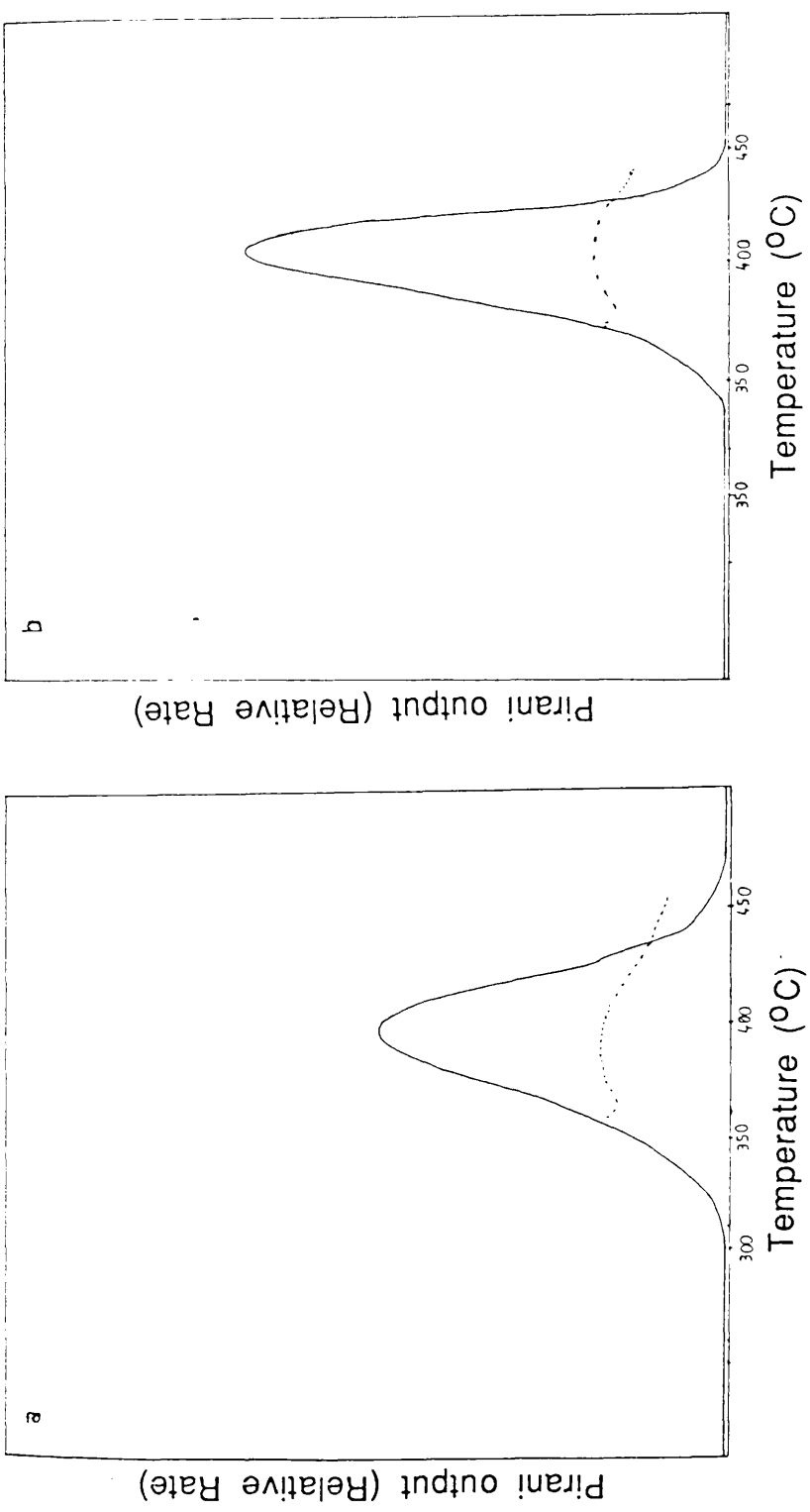


Fig. 4.1. TVA curves for homopolymers under vacuum, heating rate 10 °C/min to 500 °C. (a) PS 37 (b) PS180

Keys: ___ 0^{o}, ... $-45^{o}C$

pressure at -45 ^{o}C.

On the basis of the TVA data, the results for both polymers are really the same, not only in respect of T_{max} at 412 ^{o} and 418 ^{o}C, but also in the character of the degradation products, as revealed by their volatility in the TVA system. The only difference which is observed is in T_i (onset temperature) at 312^{o} and 345 ^{o}C for PS37 and PS180, respectively. TVA data are summarised in Table 4.1.

4.1.1. Subambient Thermal Volatilisation Analysis

The condensable volatile degradation products from polymer samples degraded to 500 ^{o}C using the TVA technique, collected in a liquid nitrogen trap, were separated by the SATVA method[29], by allowing the trap to warm up from -196^{o}C to ambient temperature in a controlled manner.The SATVA traces for PS37 and PS180 are shown in Figs. 4.2 and 4.3, respectively. The shapes of the SATVA traces are closely similar, suggesting a similarity of product composition from each degradation.

4.1.2. Product Analysis

The -196 ^{o}C condensable products of degradation, separated into fractions by the SATVA technique, were identified by infrared spectroscopy, mass spectrometry, nuclear magnetic resonance spectrometry and GC-MS techniques.

The use of several techniques was required since interpretation of the spectra is difficult due to a mixture of products. In this investigation, the minor products from degradation of polystyrene to 500 ^{o}C, present as a liquid associated with the broad peak of the SATVA trace, were examined by GC-MS. The degradation products are listed in Table 4.2.

Table 4.1 TVA Data for Anionic Polystyrene (PS37) and Free radical Polystyrene (PS180) Samples, Degraded Under Programmed Heating Conditions to 500 ^{o}C.

Polymer	T_i ^{o}C	T_{max} ^{o}C	Wt% CRF	Wt% of volatile fractions
PS37	312	412	31.5	68.5
PS180	345	418	32.1	67.9

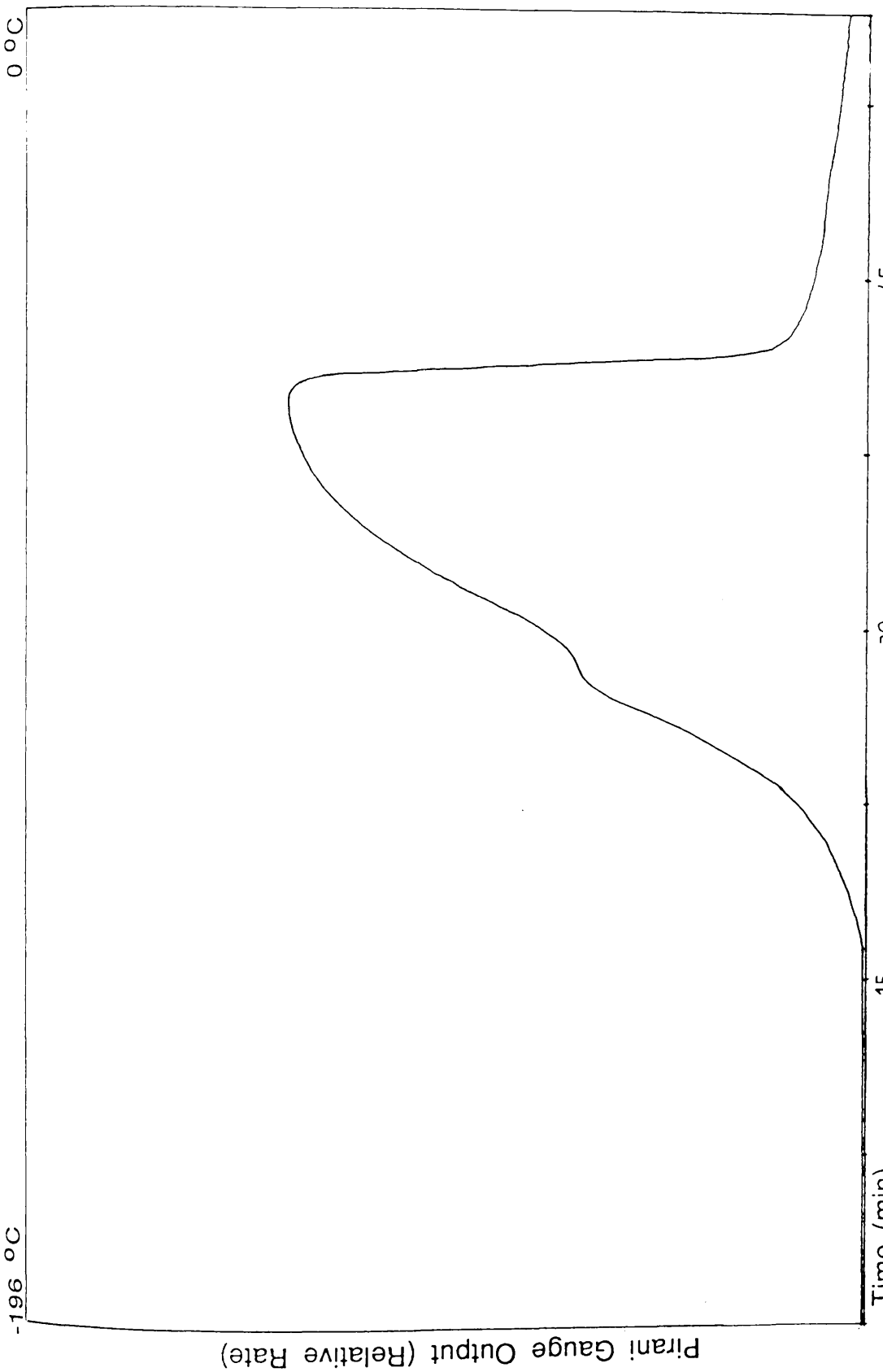


Fig. 4.2. SATVA curve for volatilisation of condensable fraction of Polystyrene (PS37) degradation products, as temperature is raised from -196° to 0 °C.

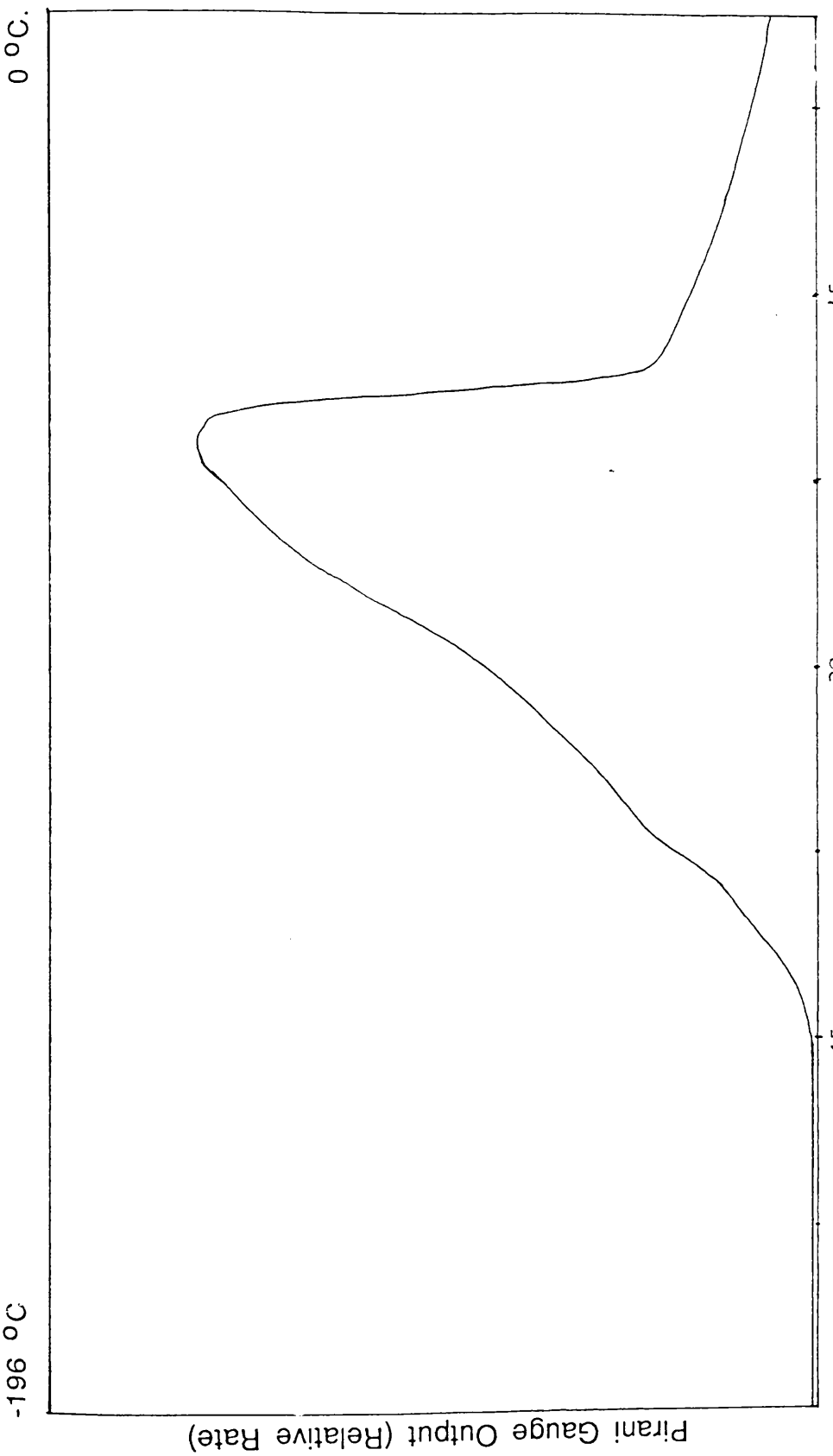


Fig. 4.3. SATVA curve for warm-up from -196 °C to 0 °C of condensable volatile Products from degradation to 500 °C under TVA conditions of Polystyrene (PS180).

Table 4.2 Products of Polystyrene (anionic and free radical) Degradation to 500°C in the TVA System Under Vacuum Using Programmed Heating.

Polymer	Volatile Liquid Condensable at -196 °C	Cold Ring Fraction
	IR, NMR, GC, GC-MS	IR, MS, TLC
PS37	Styrene Toluene ∝-methyl styrene Allylbenzene 4-phenyl-1-butene Naphthalene	Short chain fragments such as dimer, trimer, tetramer, etc. with extra methyl group
PS180	Styrene Toluene ∝-methyl styrene Allylbenzene	Short chain fragments

4.1.2.1. Condensables as Liquid Fraction

In both homopolymer samples, IR spectra (Fig. 4.4) and NMR spectra (Fig. 4.5) for this fraction are indistinguishable from that of styrene.

The liquid fractions were also subjected to GC-MS. Instrumental conditions during GC-MS analysis were as follows;

Injector temperature 250 ^{o}C, voltage 70 ev, column temperature initially 50 ^{o}C for 10 min then programmed at 5 ^{o}C/min to 200 ^{o}C, helium gas flow rate 10ml/min. The corresponding chromatograms obtained are illustrated in Figs. 4.6 and 4.7, respectively. Toluene,α-methylstyrene and allylbenzene are the volatile products next in importance to styrene, when each polymer is degraded to 500 ^{o}C in the TVA system. In the case of anionic polystyrene, isopropylbenzene and 4-phenyl-1-butene were also present as the minor liquid products. Naphthalene was also obtained, as an impurity from initiator.

4.1.2.2. Cold Ring Fraction

Cold ring fraction (light brown) products, which collected on the cooled upper part of the TVA tube, were removed using a volatile solvent. These were examined by IR, NMR and MS methods.

In both polymers (anionic and free radical) IR spectra of cold ring fractions were similar. The IR spectrum (Fig. 4.8) differed from that of the homopolymer only in the appearance of bands at 1625, 990 and 910 cm^{-1}, which are due to carbon-carbon double bond stretch and vinyl group C-H deformations. The proton NMR spectrum of the cold ring fraction illustrated in Fig. 4.9, shows additional signals at 2.3∂ and 2.72∂ which are due.to $-CH_3$ and $-CH_2$-Ar protons.

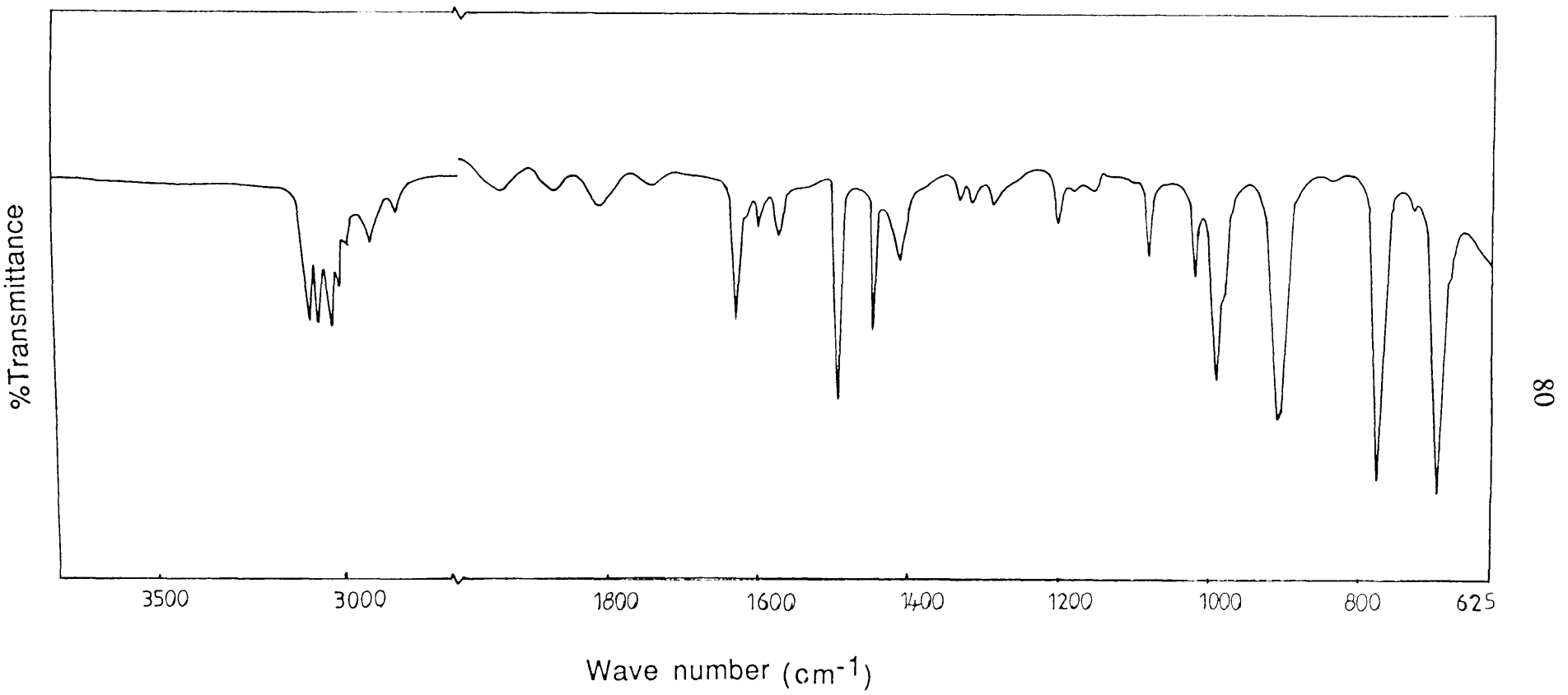


Fig. 4.4. Infrared spectrum of condensable volatile liquid fraction from degradation of polystyrene samples (PS37 & PS180) to 500 ^{o}C under TVA conditions.

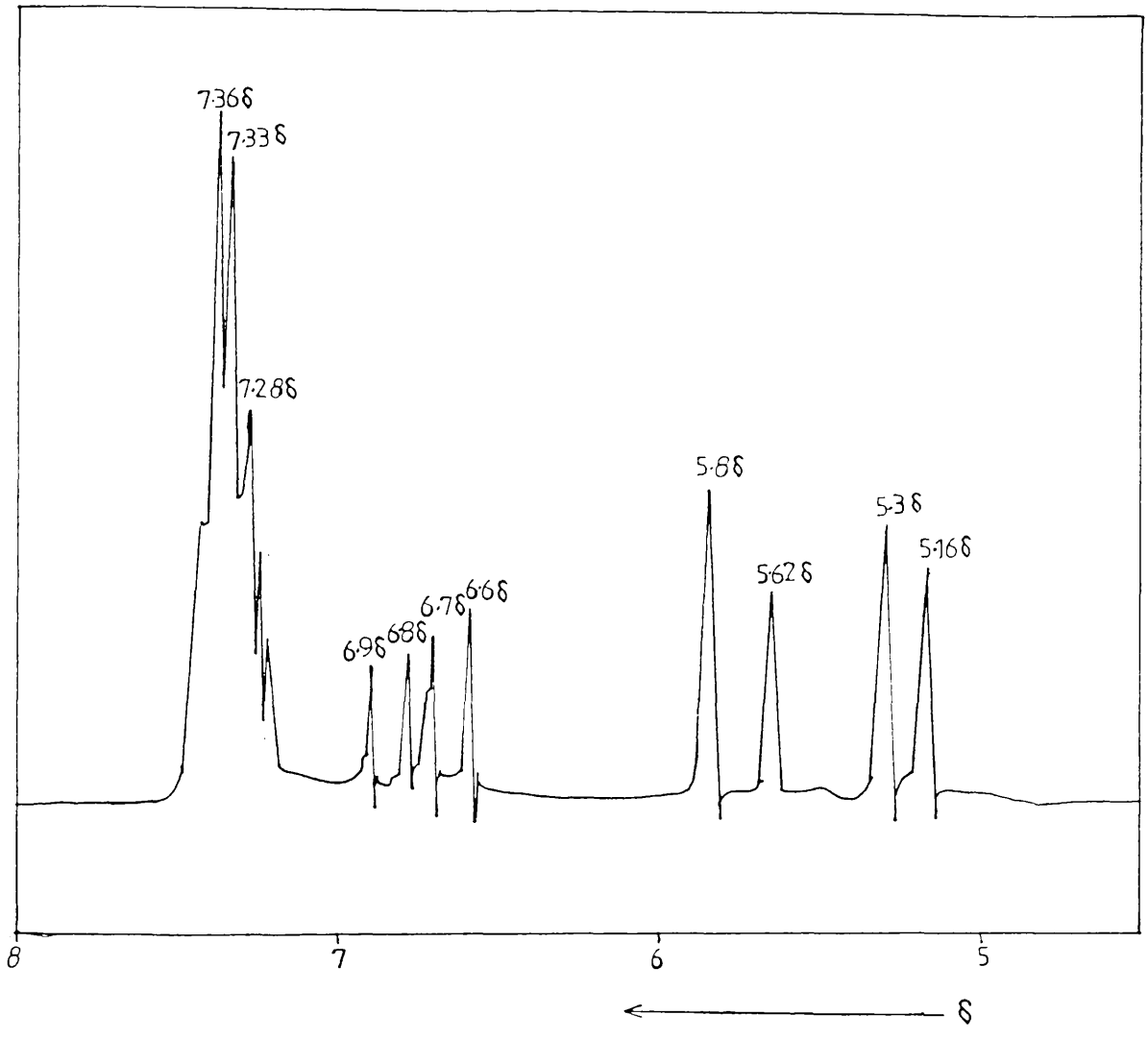


Fig. 4.5. NMR spectrum of condensable volatile liquid fraction from degradation of Polystyrene samples (PS37 & PS180) to 500 ^{o}C under TVA conditions.

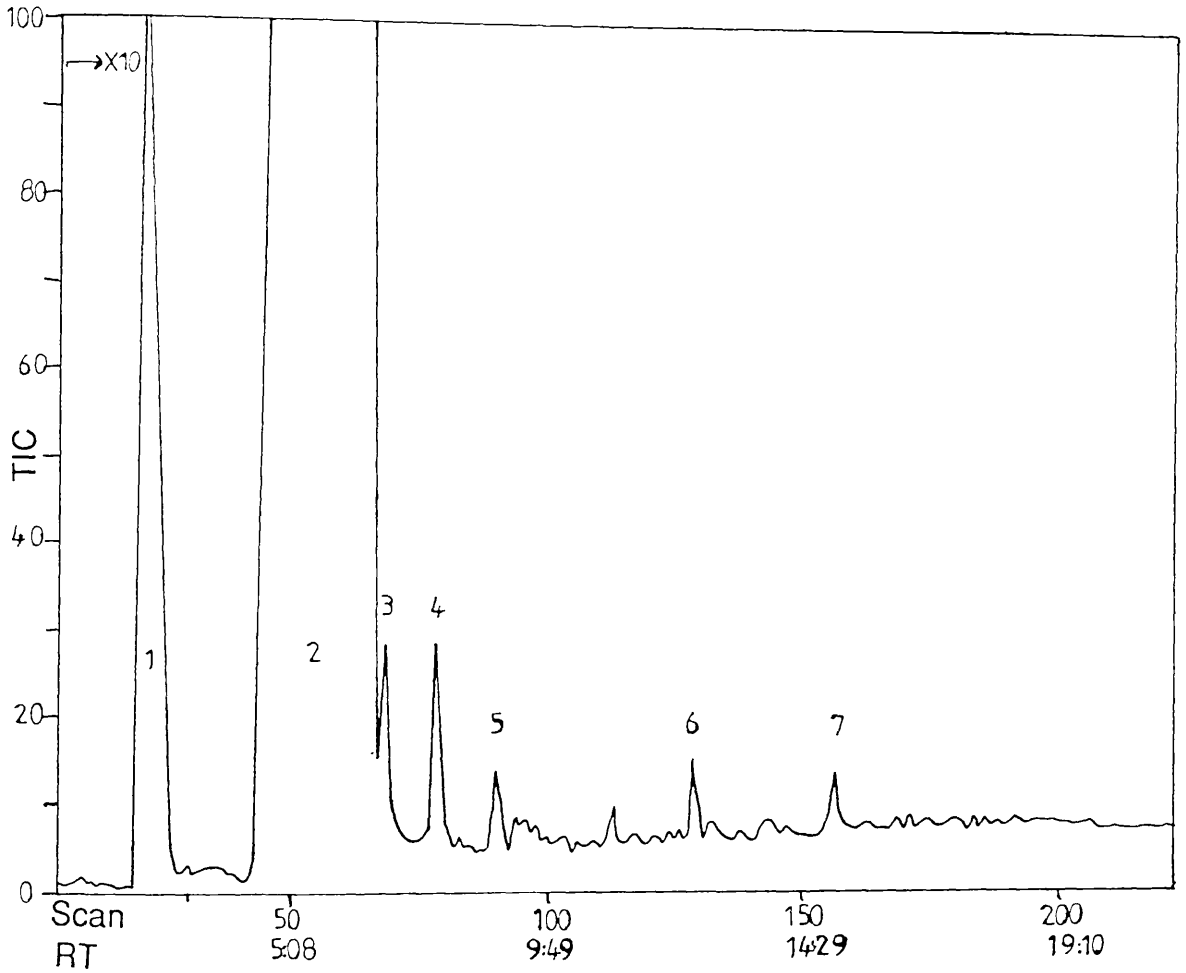


Fig. 4.6. GC data for the total volatile liquid fraction from degradation of (PS37) to 500 ^{o}C under TVA conditions.

Assignments: 1; Toluene, 2; Styrene, 3; Allylbenzene, 4; α-methylstyrene, 5; Isopropylbenzene, 6; 4-Phenyl-1-butene, 7; Naphthalene.

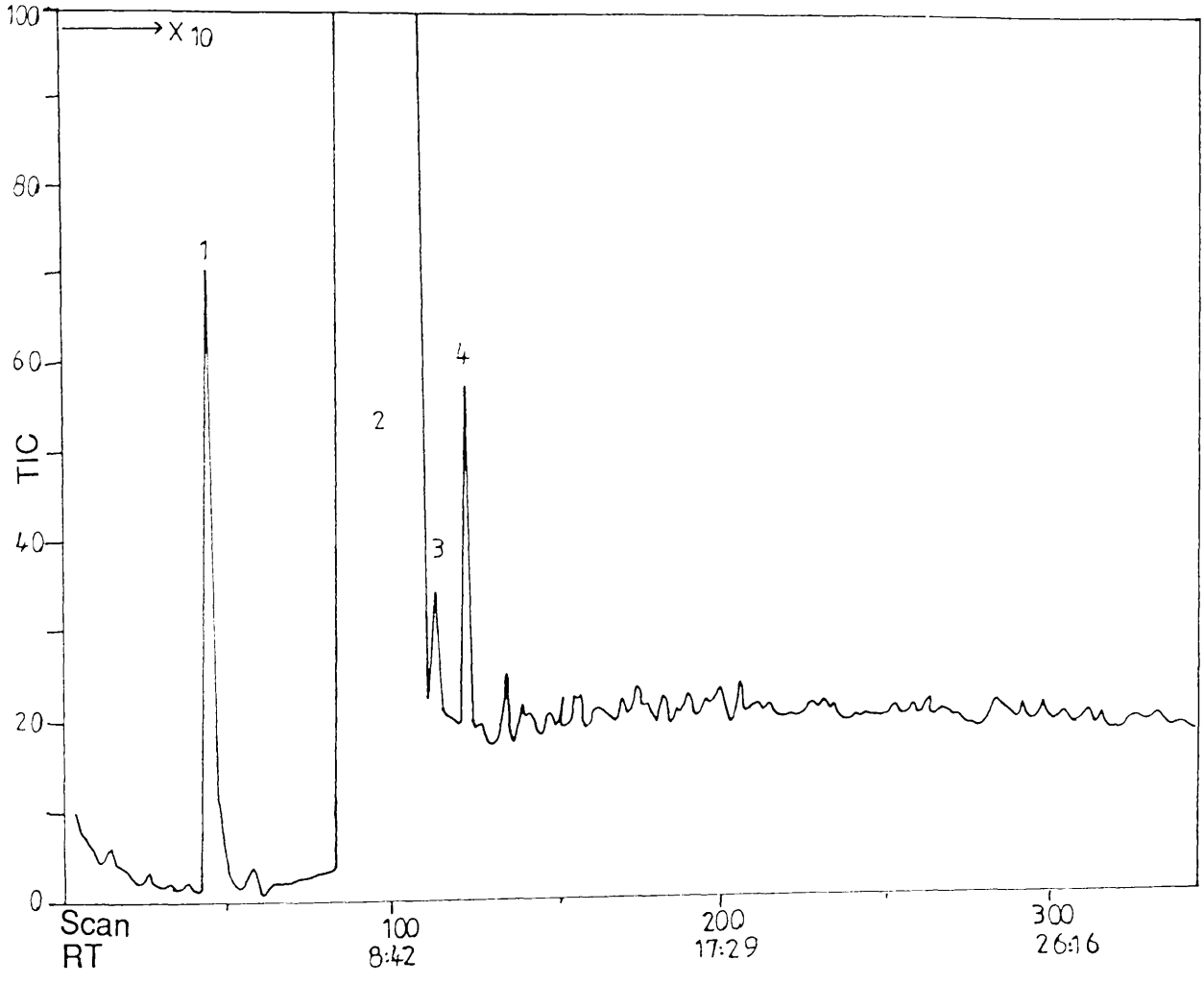


Fig. 4.7. GC data for the total volatile liquid fraction from degradation of (PS180) to 500 ^{o}C under TVA conditions.

Assignments: 1; Toluene, 2; Styrene, 3; Allylbenzene, 4; α-methylstyrene.

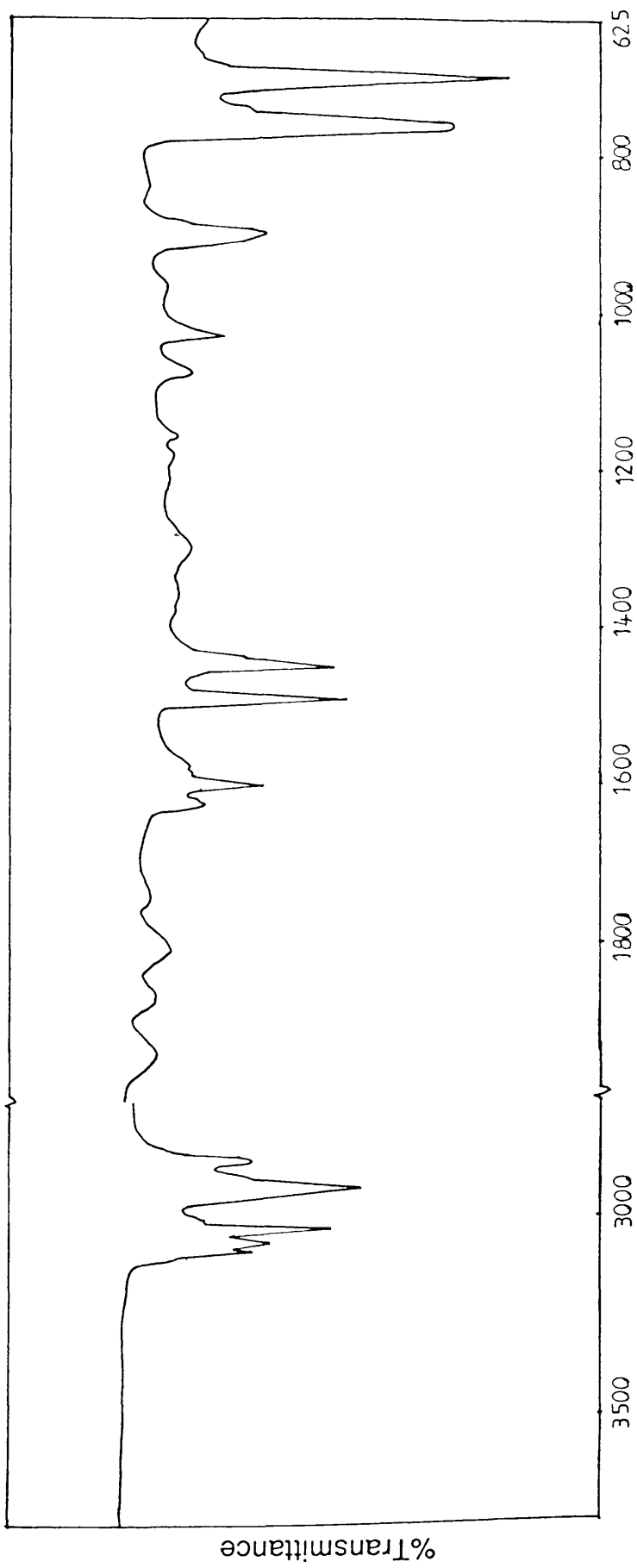


Fig. 4.8. Infrared spectrum of cold ring fraction from degradation of Polystyrene (PS37 & PS180) samples to 500 ^{o}C under TVA conditions.

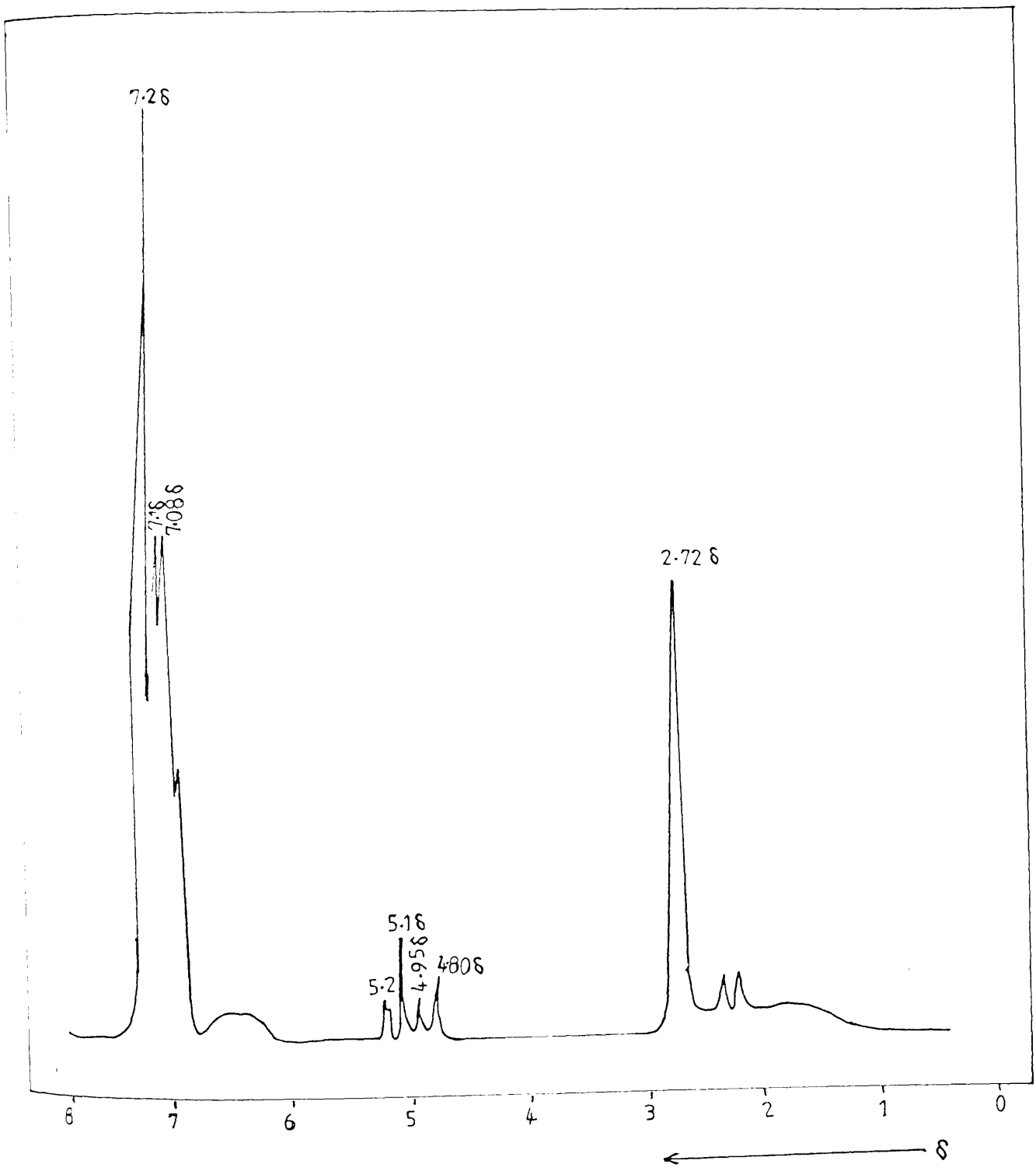


Fig. 4.9. NMR spectrum of cold ring fraction from degradation of Polystyrene (PS37 & PS180) samples to 500 ^{o}C under TVA conditions.

Preparative thin layer chromatography was carried out using n-hexane as a solvent. The three fractions separated by this technique were examined by MS. The mass spectra are shown in Fig. 4.10(a,b,c). The mass spectrometric data are consistent with the presence of dimer, trimer, tetramer and similar products with extra methyl group.

4.2. THERMOGRAVIMETRY

The TG and DTG curves obtained under dynamic nitrogen at 10 ^{o}C/min heating rate, shown in Fig. 4.11 (a,b), for anionic and free radical polystyrene samples indicates that the volatilisation process occurs in a single stage. This begins at approximately 337 ^{o}C with rate maximum at 420 ^{o}C in the former case, whereas volatilisation begins at approximately 355 ^{o}C with rate maximum at 426 ^{o}C in the latter case. In each case there was no residue. The small discrepancy between the TVA and TG rate trace maxima is explained by the more efficient product removal under vacuum.

4.3. DIFFERENTIAL THERMAL ANALYSIS

In anionic polystyrene and free radical polystyrene the position and the shape of DTA minima at 416 ^{o}C in former and 420 ^{o}C in the latter (Fig. 4.12) agree well with the DTG curves. DTA thermograms obtained under dynamic nitrogen at 10^{o}C/min and confirm the endothermic nature of the bond scission process. DTA, TG and DTG data are compared in Table 4.3.

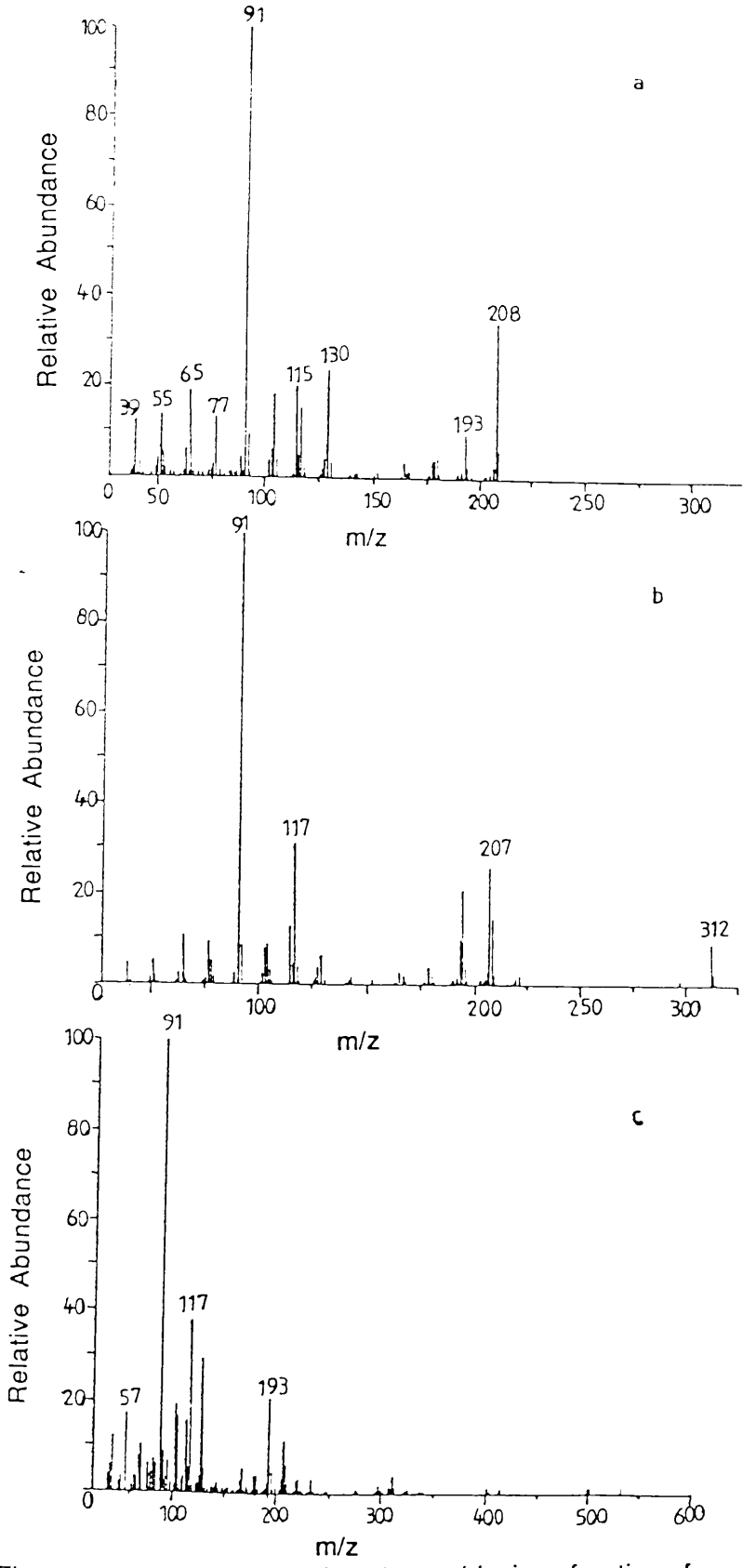


Fig. 4.10. MS spectra for the cold ring fraction from degradation of Polystyrene (PS37 & PS180), after preparative thin layer chromatography for (a) upper spot (b) middle spot (c) lower spot.

Table 4.3 DTA, TG and DTG Data for Anionic Polystyrene (PS37) and Free radical Polystyrene (PS180) Samples Under Dynamic Nitrogen.

	TG		DTA			DTG	
Polymer	T(1%) °C	T(50%) °C	Peak temp., °C	Temp. range, °C	Type	Peak temp., °C	Temp. range, °C
PS37	320	405	416	295-450	Endo-thermic	420	335-470
PS180	350	410	422	300-450	' ' '	426	350-470

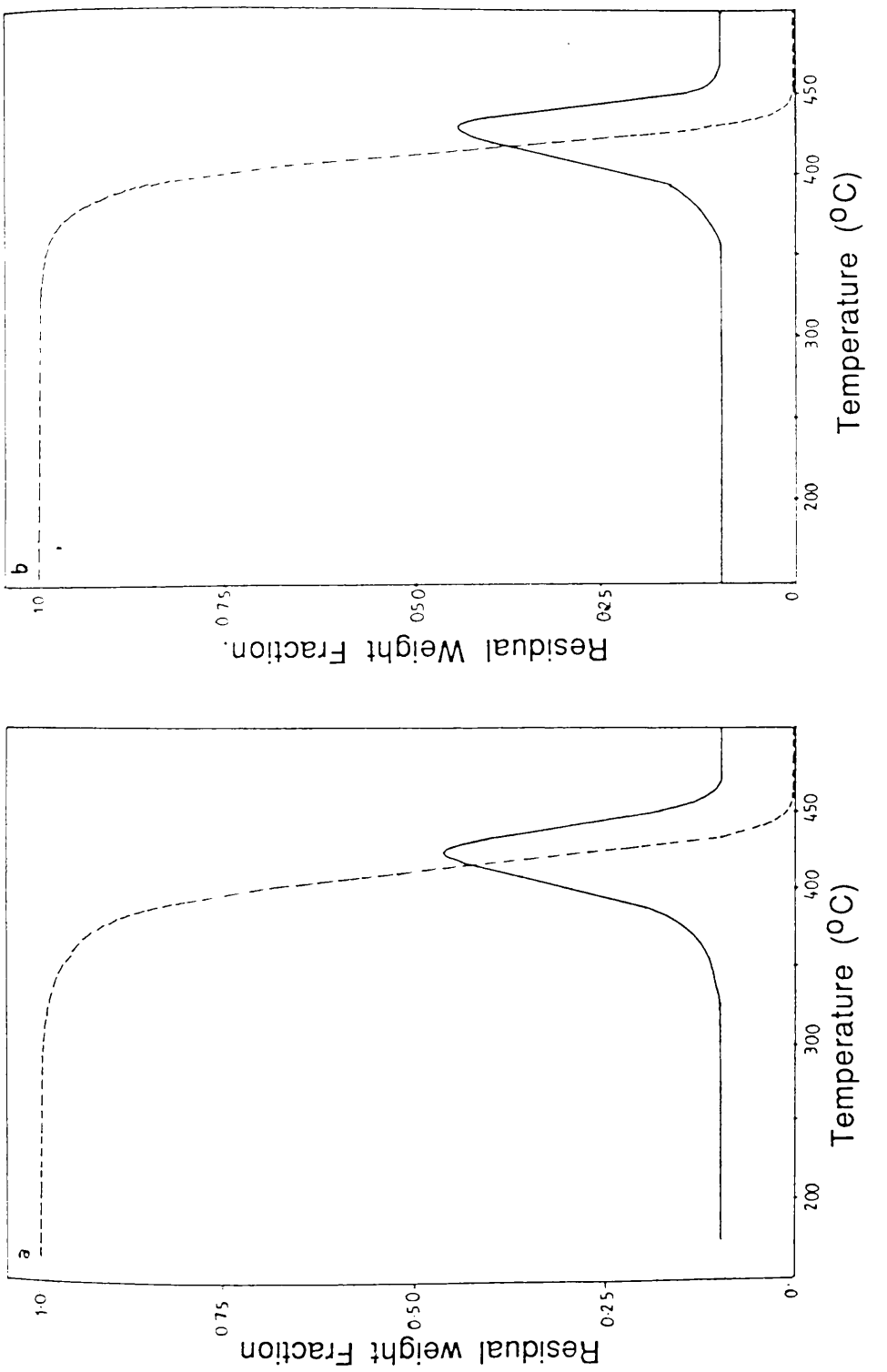


Fig. 4.11. TG and DTG curves for Polystyrene samples.

(a) PS37 (b) PS180

Keys: - - -DTG, ____ TG.

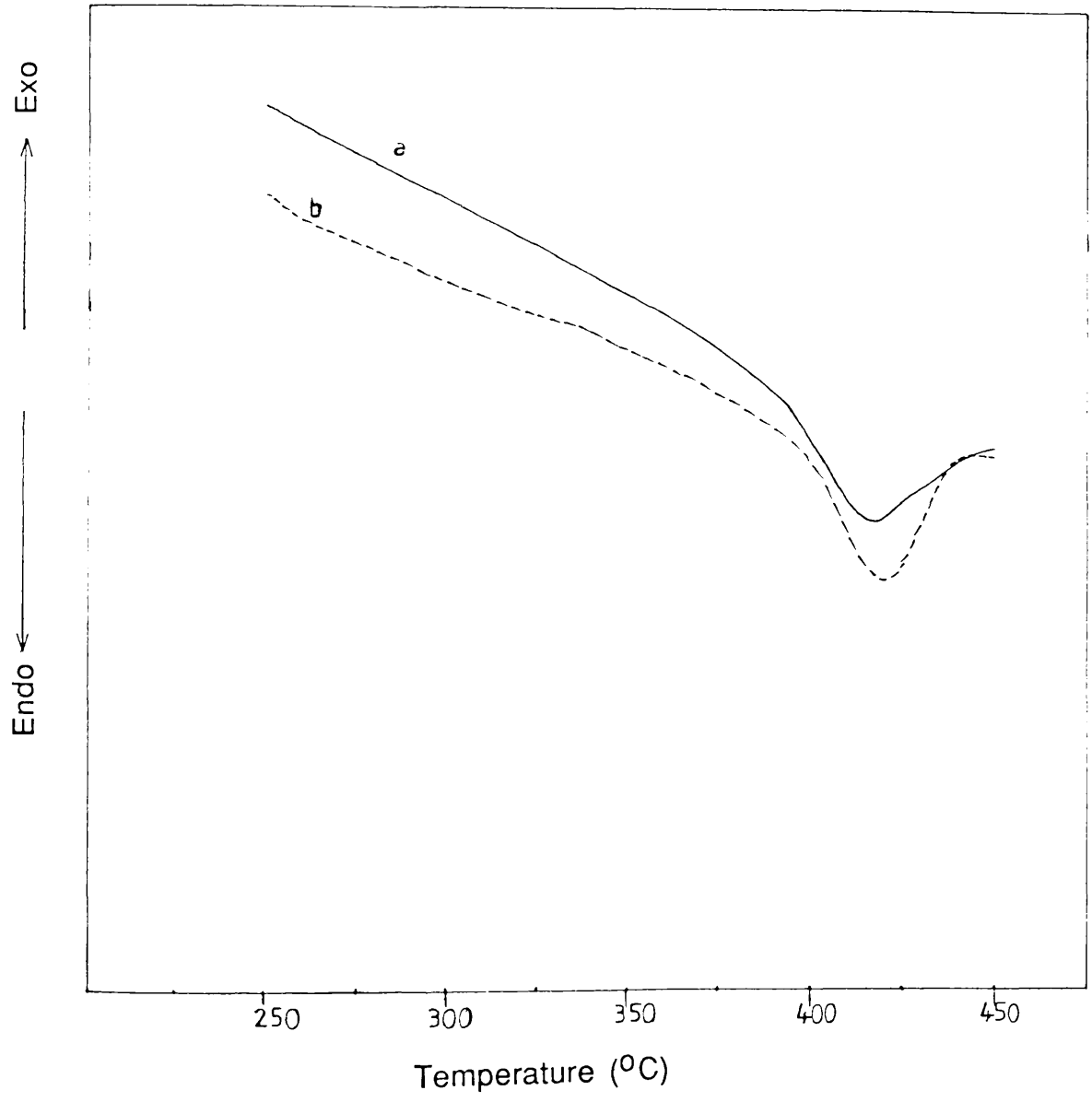


Fig. 4.12. DTA curves for Polystyrene samples under dynamic nitrogen atmosphere, heating rate 10 °C/min.
(a)PS37 (b) PS180

CHAPTER FIVE

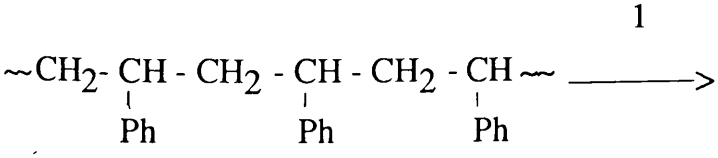
DETAILED STUDY OF POLYSTYRENE VOLATILE PRODUCTS

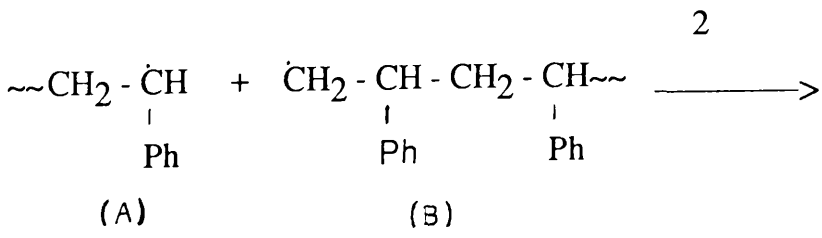
In this chapter, investigations using TVA, TG, DTG and DTA techniques of the thermal stability of anionically prepared polystyrenes and the examination of the volatile products of degradation under TVA conditions at 300°, 350° and 420 °C using GC-MS, are described. Some comparative data for polystyrene made by the free radical route are included.

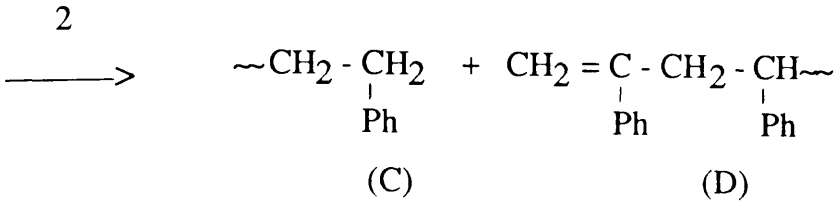
1. INTRODUCTION

The main features of the degradation of polystyrene, established by various workers over many years, have been considered in Chapter Four. Certain aspects of the degradation mechanism still remain the subject of discussion.

Below 300 °C, random scission (reaction 1) and disproportionation of the macroradicals formed (reaction 2) account for the observed molecular weight decrease.[167]



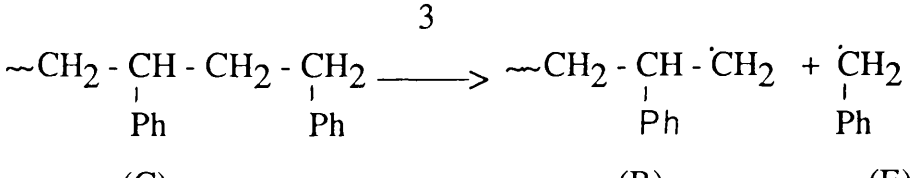




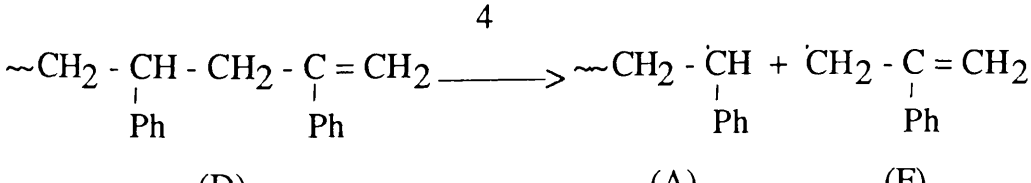
(C) (D)

Since volatilisation is not significant below 300 °C, it follows that chain ends (C) and (D) must be stable in this temperature region.

Initiation of production of volatile products from polystyrene above 300 °C results from homolysis at random or near (C) and (D) type ends. The first of these is as already shown in reaction 1; the other two possibilities are given in reactions 3 and 4:

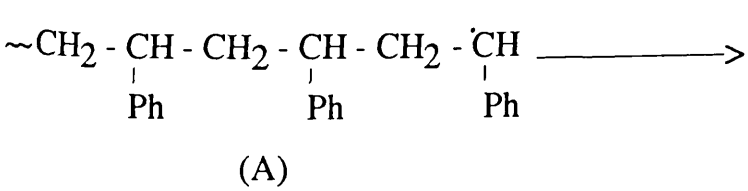


(C) (B) (E)

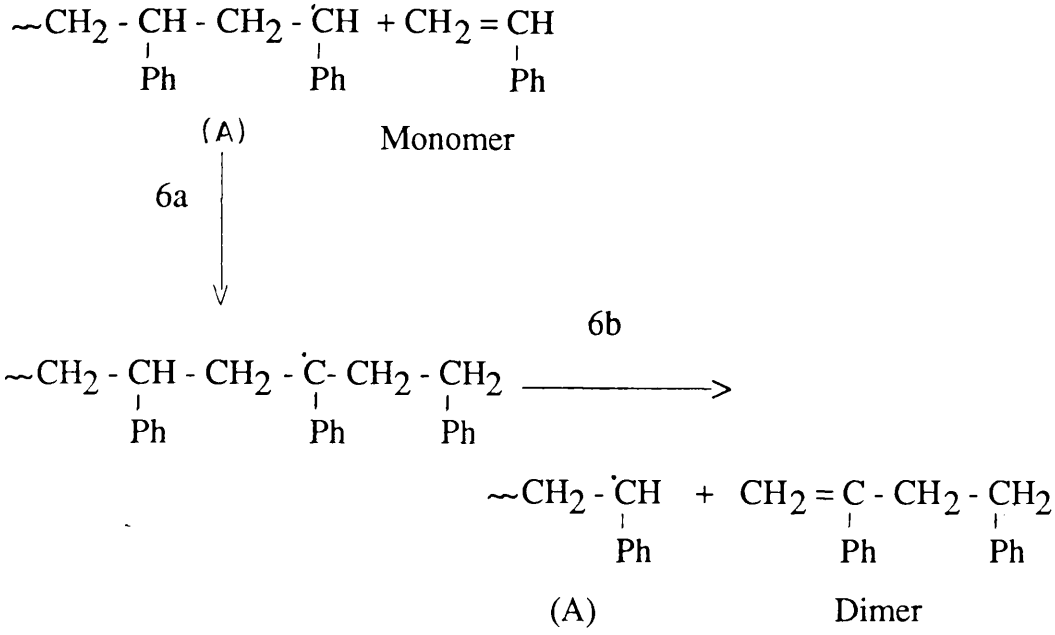


(D) (A) (F)

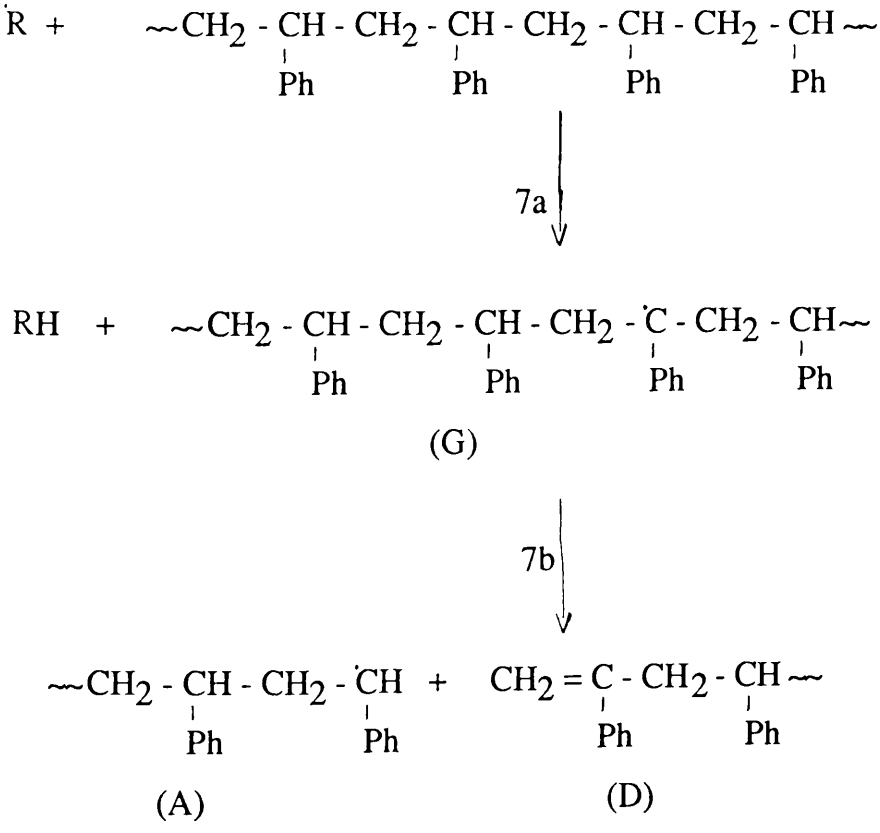
Depropagation is believed[21,105] to involve only macroradical (A), reaction 5, and the same radical is also involved in a competing backbiting intramolecular transfer reaction, shown as reaction 6, which leads to dimer, etc;



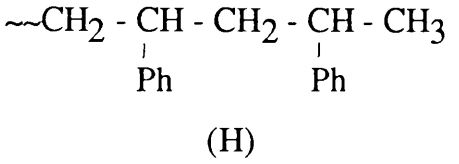
(A)



The fall in molecular weight may result from random scission or from intermolecular transfer. The latter process is illustrated in reaction 7:



Each of the radicals (A), (B), (E) and (F) could participate as $\dot{R}$ in the H abstraction process of reaction 7a. The tertiary macroradical (G) thus produced, sometimes referred to as an on-chain radical, undergoes scission (reaction 7b) to give macroradical (A) and a vinylidene end (D). When radical (B) reacts in this way, a methyl end (H) results, whereas if radical (A) participates in this way, a benzylic end (C) is formed.



(H)

There are several modes of formation of the minor volatile products, toluene and ∝-methylstyrene, which will be considered subsequently.

The unsaturated chain end (D) has been thought by various workers to be the site at which depolymerisation is initiated by the formation of the macroradical (A) in reaction 4. This suggestion has been challenged by others,[106] who propose that the formation of radical (A) by random scission and especially following intermolecular transfer provides the principal route to the formation of volatile products.

In polystyrene made by the anionic route, the benzylic end (C) has also been identified as a site for the initiation of depolymerisation.[105,106] Little attention has so far been devoted to the possible effect on the degradation of the presence of head to head linkages in polystyrene samples made anionically using an initiator such as sodium naphthalenide.

In the subsequent discussion, the thermal behaviour of polystyrene samples having different molecular weights, has been studied using DTG, TG and TVA. The degradation studies were carried out using two approaches, programmed

heating at 10 ^{o}C/min to 500 ^{o}C and isothermal heating, at 300^{o}, 350^{o} and 420^{o}C.

2. THERMAL STABILITY

Polystyrene samples having molecular weight 12,000 and 53,000 were prepared anionically as described in Chapter Three. In addition, polystyrene samples of molecular weight 233,000 and 618,000, also prepared anionically, supplied by the Mellon Institute were studied. The polymers used in this investigation are listed in Table 5.1.

2.1. Differential Thermal Analysis Under Nitrogen (10 ^{o}C/min)

DTA curves for PS12, PS53, PS233 and PS618 are shown in Fig. 5.1. The DTA data for these samples are nearly identical and confirm the endothermic nature of the bond scission process.

2.2. Thermogravimetry Under Nitrogen (10 ^{o}C/min)

The TG curves for PS12, PS53, PS233 and PS618 are shown in Fig. 5.2. All the curves show the single step nature of the volatilisation process. The initial weight loss temperature (1% wt.loss) is different in these polymer samples. This suggests that the initial temperature of volatilisation depends on the concentration of chain ends, which is much higher in the lower molecular weight samples PS12 and PS53. TG and DTA data are summarised in Table 5.2.

2.3. Thermal volatilisation Analysis

TVA traces for PS12, PS53, PS233 and PS618 are shown in Fig. 5.3(a,b,c,d). The TVA experiments were performed under vacuum, heating rate 10 ^{o}C/min to 500 ^{o}C.

Table 5.1 Polystyrene Samples

Sample	Type	$\bar{M}n$	$\bar{M}w/\bar{M}n$
PS12	Anionic	12,000	1.4
PS53	Anionic	53,000	1.3
PS233[a]	Anionic	233,000	1.06
PS618[a]	Anionic	618,000	1.09

[a]Mellon Institute Sample

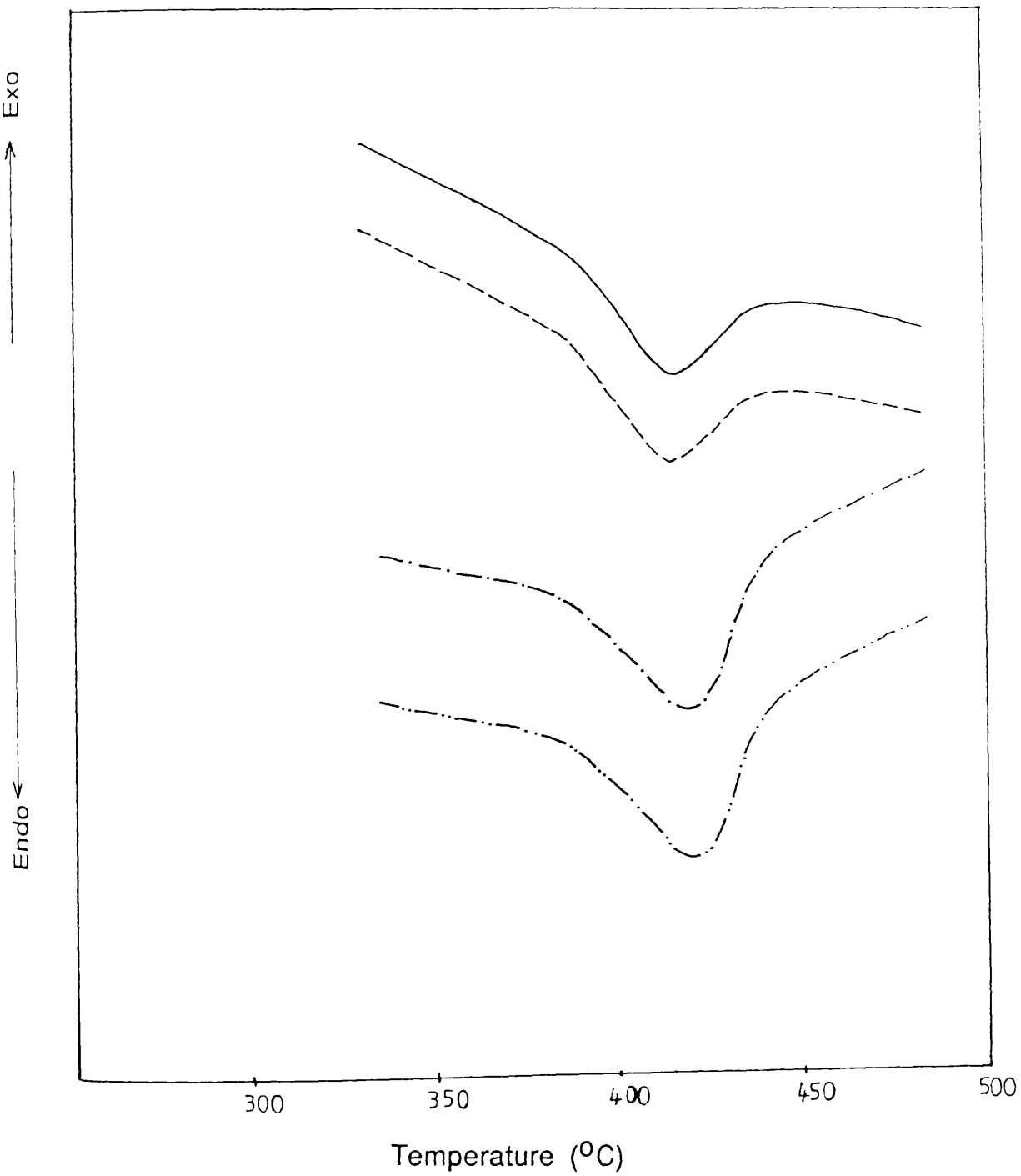


Fig. 5.1. DTA curves for anionic Polystyrene samples (dynamic nitrogen, heating rate 10 °C/min)

Keys: ____ PS12, - - - PS53, _ . _ . _ PS233, _ . . _ . . PS618

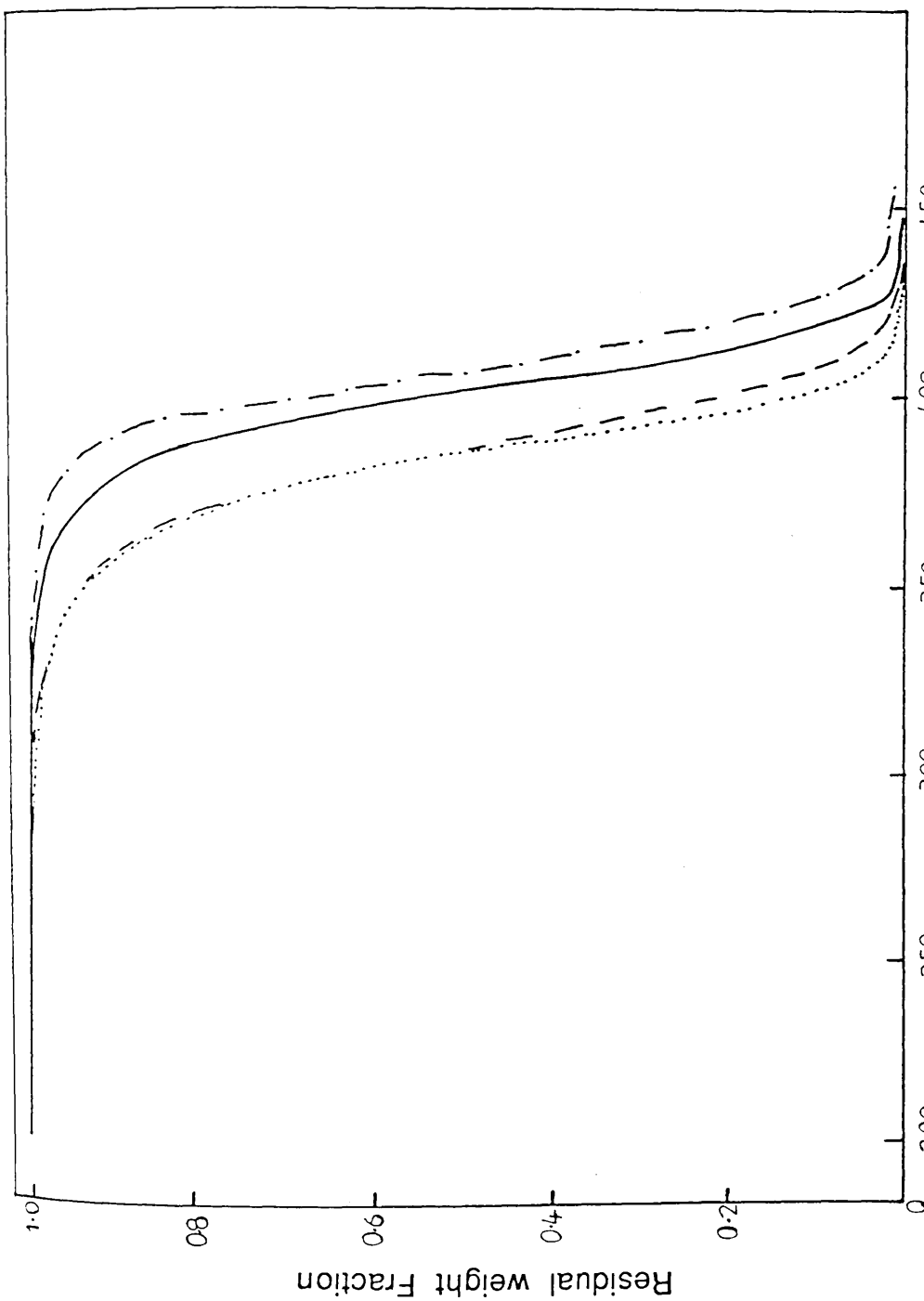


Fig. 5.2. TG curves for anionic Polystyrene samples (dynamic nitrogen rate 10 °C/min).

Keys:.....PS12, - - -PS53, ____ PS233, - · - · - PS618

Table 5.2 TG and DTA Data for Polystyrene Samples.

Sample	TG data		DTA data	
	T(1%) ^{o}C	T(50%) ^{o}C	$T_{(i)}$ ^{o}C	$T_{(max)}$ ^{o}C
PS12	305	385	310	415
PS53	307	385	310	415
PS233	325	403	327	418
PS618	350	405	360	420

A single stage decomposition is indicated, with onset of volatilisation (T_i) above 300 °C and rate maximum (T_{max}) between 403° and 416 °C. The onset and maximum rate temperatures as determined by TVA and DTG are listed in Table 5.3. Althought the small difference in the rate maxima in the TVA traces for these polymers is somewhat influenced by the initial molecular weight, the effect of molecular weight on the T_i is considerable. This suggests that the initial temperature of volatilisation is dependent on the concentration of the chain ends.

The "limiting" rate behaviour observed in the -45 °C curve has been discussed previously in Chapter Four. In this case it indicates that a major product of quite low volatility (in fact, styrene) is present.

2.4. Isothermal Degradation at 300 °C

Polystyrene samples were degraded isothermally at 300 °C under normal TVA conditions. The volatile materials were estimated gravimetrically.

All of the samples contained benzylic chain ends initially. In Fig. 5.4 the extent of volatilisation as a function of time is illustrated and clearly indicates the lower stability as the initial molecular weight of the polymer becomes smaller. Similar behaviour has been noted by other investigators.[106,107] These workers seem to agree that volatilisation depends on both random chain scission and end initiated unzipping. Random scission, when followed by disproportionation of the macroradicals, leads to the benzylic (C) and vinylidene (D) end structures (see reactions 1 and 2).

The interpretation of the molecular weight decrease in polystyrene degradation and its relation to volatilisation has been an area of controversy for many years as noted in the literature review in Chapter Four.

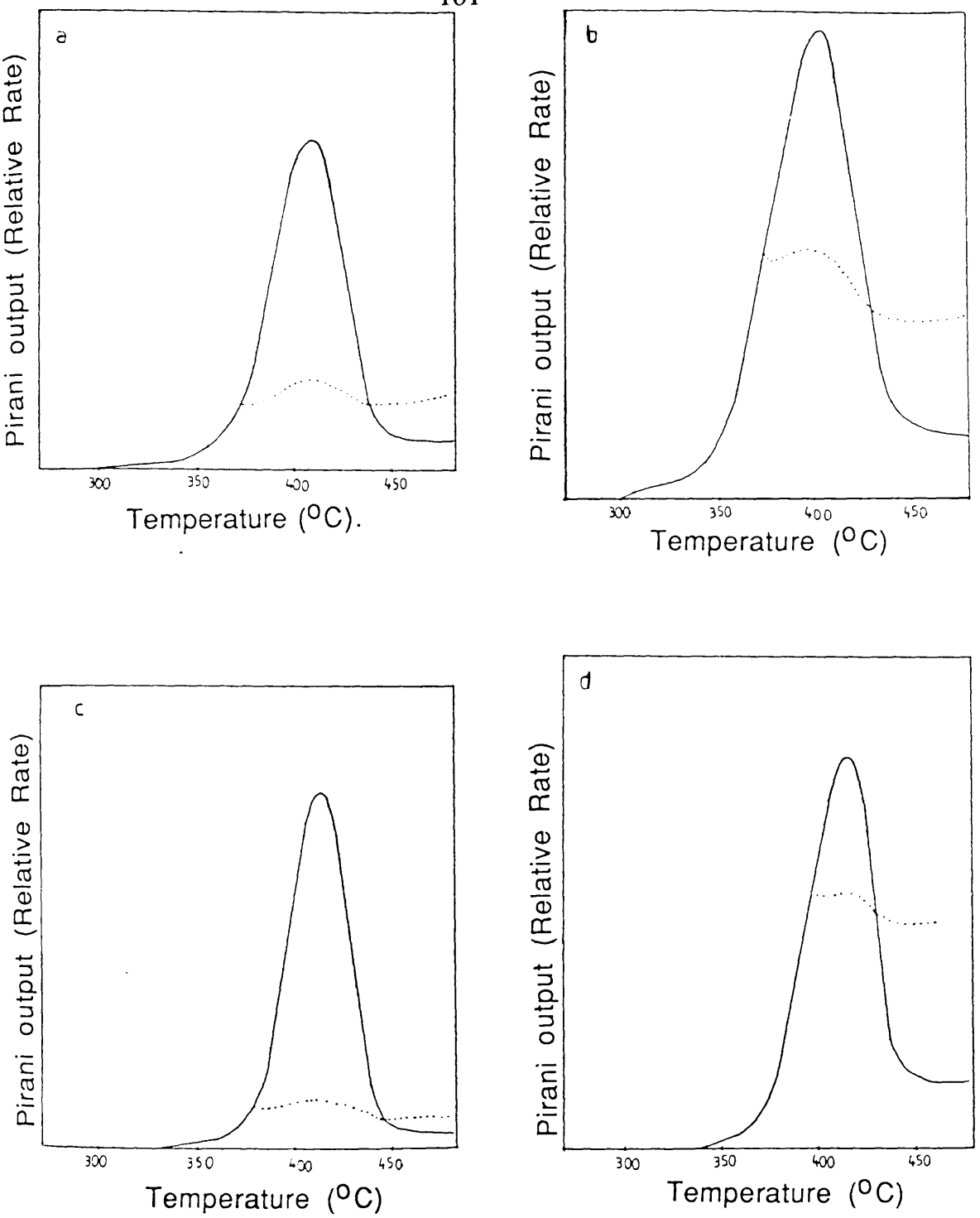


Fig. 5.3. TVA curves (vacuum, heating rate 10 °C/min) for anionic Polystyrene samples. _____ 0°, ...-45 °C.

(a) PS12, (b) PS53, (c) PS233, (d) PS618.

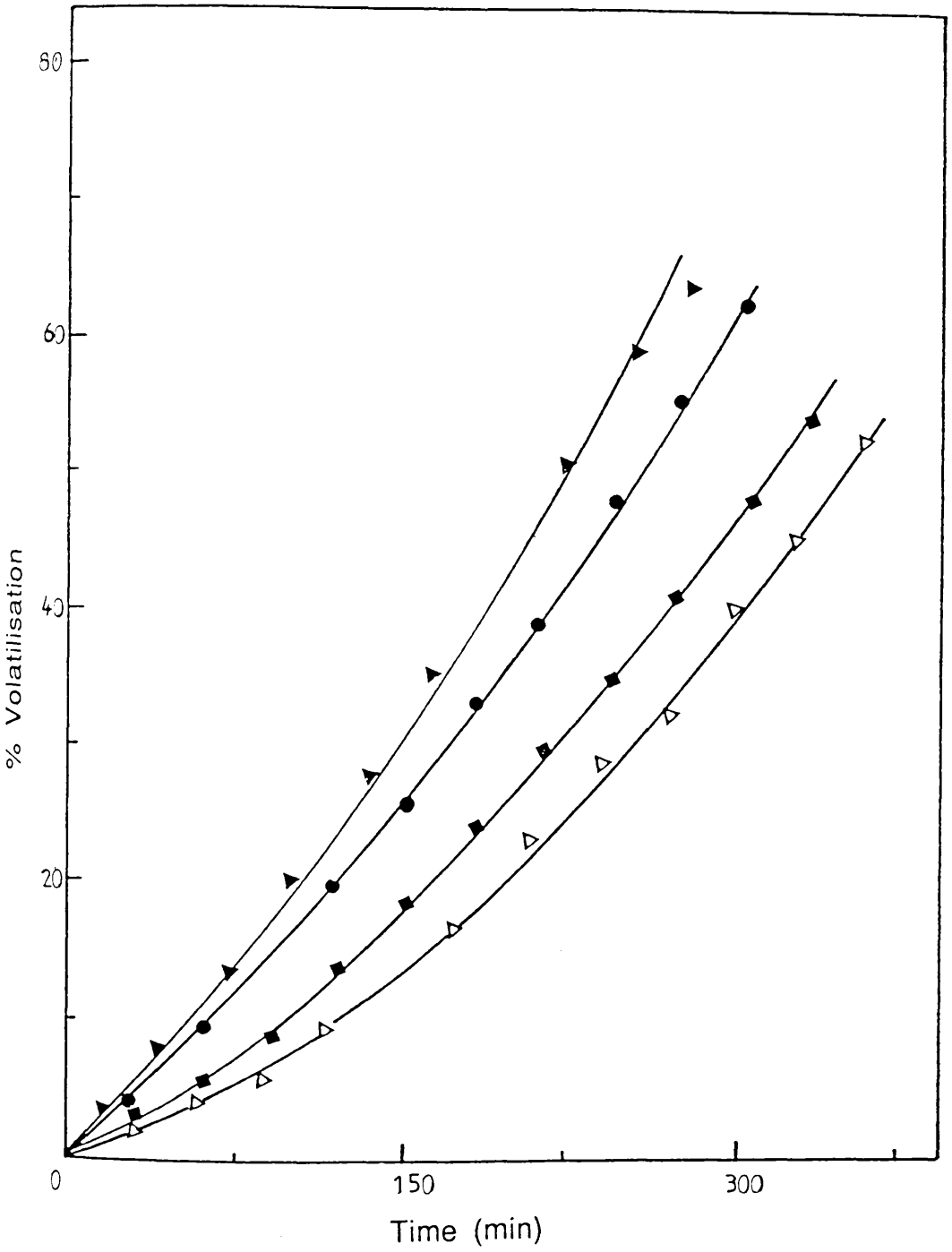


Fig. 5.4. Gravimetric data for volatilisation of anionic Polystyrene samples at 300 ^{o}C under vacuum in the TVA system as a function of time.

Keys; ▲ PS12, • PS53, ■ PS233, Δ PS618

Table 5.3 Stability Data for Polystyrene samples

Sample	TVA data		DTG data	
	$T_{(i)}$ °C	$T_{(max)}$ °C	$T_{(i)}$ °C	$T_{(max)}$ °C
PS12	307	403	325	412
PS53	343	411	335	415
PS233	357	411	350	420
PS618	361	416	360	420

Several polystyrene samples were heated isothermally at 300 °C and the relative proportions of volatile liquid to CRF products over a wide range of extents of volatilisation was examined. If inter- and intramolecular transfer are occurring throughout the degradation, as most workers have supposed, it would be expected that the volatile liquid/CRF ratio would remain constant, as several workers have reported. This would not, however, be consistent with the reasoning of Ide et al.,[118] which would suggest that a larger proportion of the CRF should be formed in the later stages of reaction than during the initial molecular weight decrease, since intermolecular transfer would be a major alternative reaction of the depropagating radical only in the earlier stages of volatilisation.

The volatile liquid/CRF ratio determinations for PS12, PS53, PS233 and PS618, obtained isothermally at 300 °C under normal TVA conditions are illustrated in Fig. 5.5. The data are based on gravimetric determinations of CRF and residue, the volatile liquid fraction being calculated by difference from the initial sample weight. Several features are apparent. For each of the polystyrene samples, the ratio becomes nearly constant after 25% volatilisation. The initial values of the ratio, however, are significantly higher and the larger the original molecular weight of the polymer, the larger is the initial ratio, which reaches a value of 5.0 for PS618 at 1.5% volatilisation.

These results imply that in the early stages of polystyrene degradation, volatile liquid fraction production greatly exceeds CRF production, but at extents of volatilisation greater than 30%, CRF production equals or exceeds volatile liquid formation.

The volatile liquid/CRF ratio has been measured by other workers and there are substantial discrepancies in the reported values. For degradation temperatures up to 425 °C under vacuum, Grassie and Kerr,[108] Madorsky et al.,[109] Straus and

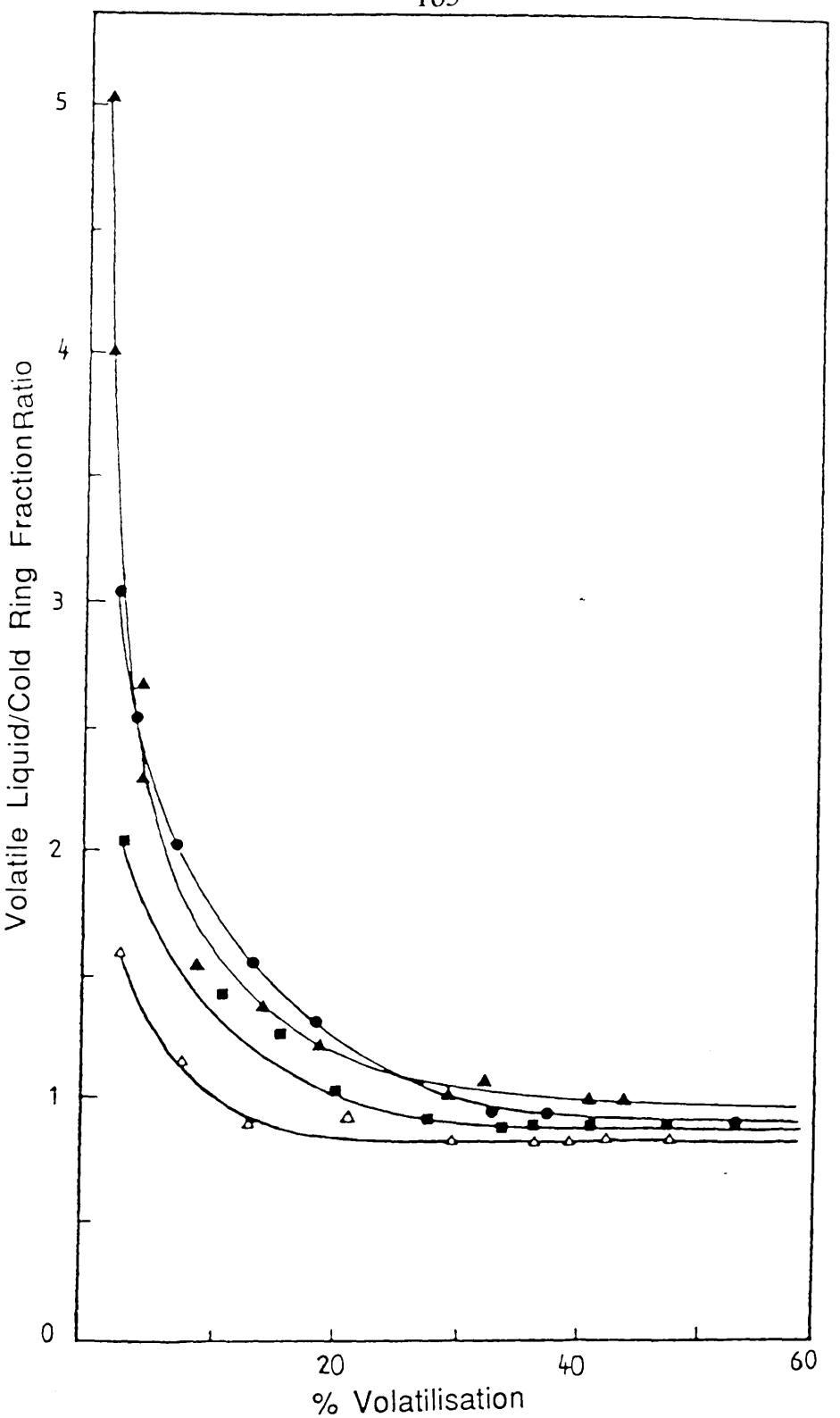


Fig. 5.5. Volatile liquid/cold ring fraction ratio for anionic Polystyrene samples as a function of % volatilisation, based on gravimetric data obtained from isothermal degradation at 300 ^{o}C under vacuum in the TVA system. The ratios shown on the ordinate are instantaneous values based on product evolution in the interval from the previous point.

Keys: Δ PS12, ■ PS53, • PS233, ▲ PS618.

Madorsky,[110] Lehman and Brauer,[111] McNeill et al.[29] and McNeill and Stevenson[112] obtained data leading to values of 0.67, 0.71, 1.23, 2.5 and 1.8, respectively. The first two results are for lower degradation temperatures than the other results quoted, which are based on experiments at 380°-425 °C. Madorsky and Straus, however, found no difference in the ratio over the temperature range from 336 ° to 375 °C. The larger ratios correspond with much higher monomer yields, which were only in the range of 40% in Grassie's and Madorsky's experiments, but 60% or more in the other cases. There have been reported of much higher monomer yields in polystyrene degradations at high temperatures.[113-115] It appears likely, therefore, that the ratio is dependent not only on extent of reaction, as the results of this study show, but also on temperature.

McNeill and Stevenson[112] used the same technique as in the present investigation and have reported volatile liquid/CRF ratios of 1.9, 1.8 and 1.7 at 68.6, 88.8 and 96.5% volatilisation, respectively, at 380 °C, these values being based on ratios of overall yields of the fractions. Therefore the values obtained at 380 °C differ from those at 300 °C.

A variation of the volatile liquid/CRF ratio with extent of volatilisation is not consistent with intramolecular transfer occurring with equal ease over the whole volatilisation range. The present studies suggest that intramolecular transfer is less easy initially, especially for samples of high initial molecular weight.

These results can be rationalised in terms of the effect of melt viscosity on radical mobility at a given degradation temperature. The higher the melt viscosity, the more difficult will be the backbiting process which leads to the formation of CRF products. Monomer production, however, is not dependent on chain mobility and will be unimpeded. At high melt viscosity, the chain entanglements which would hinder intramolecular transfer would also facilitate intermolecular transfer, with

consequent enhancement of chain scission. It is suggested that intermolecular transfer of the terminal macroradical is only of major importance under such conditions. Conversely, it is also argued that backbiting processes, which are intramolecular, occur very much more readily than intermolecular transfer at lower melt viscosity. Hydrogen abstraction by small radicals is also likely to be favoured in the earlier stages, since the ease of diffusion of these radicals out of the melt will increase as the melt viscosity falls.

2.5. Product Analysis

The various degradation products, consisting of residue, liquid fraction, and cold ring fraction, were examined after degradation of polystyrene samples under TVA conditions. The product analysis was carried out spectroscopically as described in Chapter Four.

2.5.1. Condensables as Liquid Fraction

There is general agreement that in addition to the major product, styrene, for which yields of between 40 and 60% are reported below 400 ^{o}C, the most important minor products are toluene (1-2%) and α-methylstyrene (about 0.5%). The relationships of minor product formation to degradation temperature is less well documented.

In this investigation, minor products composition has been examined by GC-MS for polystyrene degraded isothermally at 300^{o}, 350^{o} and 420 ^{o}C under TVA conditions. A typical chromatogram for products of degradation of a 100 mg PS12 sample at 300 ^{o}C for 15 min is shown in Fig. 5.6. Peaks in the chromatogram after that due to styrene are magnified by a factor of five. The same PS sample was then heated successively for 15 min at 350 ^{o}C and 15 min at 420^{o}C and the corresponding, chromatograms are shown in Figs. 5.7 and 5.8,

respectively.

The products at each degradation temperature are listed in order of importance in Table 5.4. The identification of the products from the mass spectrum at each peak is based on comparison with the spectra of authentic samples or the fragmentation patterns of the compounds in library mass spectra,[116] as indicated. Toluene is clearly the volatile product next in importance to styrene at all temperatures. It can be formed by two routes. The first is intermolecular transfer of radical (E) as R in reaction 7a. The second is disproportionation of radical (B) and (E) following reaction 3. In the case of α-methylstyrene, more is formed at 350 ^{o}C than at 300^{o}C but at 420 ^{o}C the yield again falls. This product could be formed by reaction of radical (F) in reaction 7a or by disproportionation of radical (A) and (F) following reaction 4. It could also result, however, by elimination from radical (B), also producing radical (A), as shown in reaction 8;

$$\sim CH_2 - \underset{\underset{Ph}{|}}{CH} - CH_2 - \underset{\underset{Ph}{|}}{CH} - CH_2 \xrightarrow{8} \sim CH_2 - \underset{\underset{Ph}{|}}{\dot{C}H} + CH_2 = \underset{\underset{Ph}{|}}{C} - CH_3$$

(A) α-methylstyrene

Whichever routes of formation of toluene and α-methylstyrene are important, these products derive ultimately from the initial chain scission, the former from the (A) end and the latter from the (B) end. The data in Table 5.4 show that the yield of toluene is greater than that of α-methylstyrene.

At 300 ^{o}C, 1-methylindene is produced from PS12 in comparable amount to α-methylstyrene, at 350 ^{o}C it is still a significant minor product but the production is less than that of α-methylstyrene, and at 420 ^{o}C it is absent. At 350 ^{o}C, there is an additional group of minor products not formed at all either at 300 ^{o}C or at 420^{o}C. Allylbenzene (3-phenylpropene) is present in significant quantities only at 420 ^{o}C.

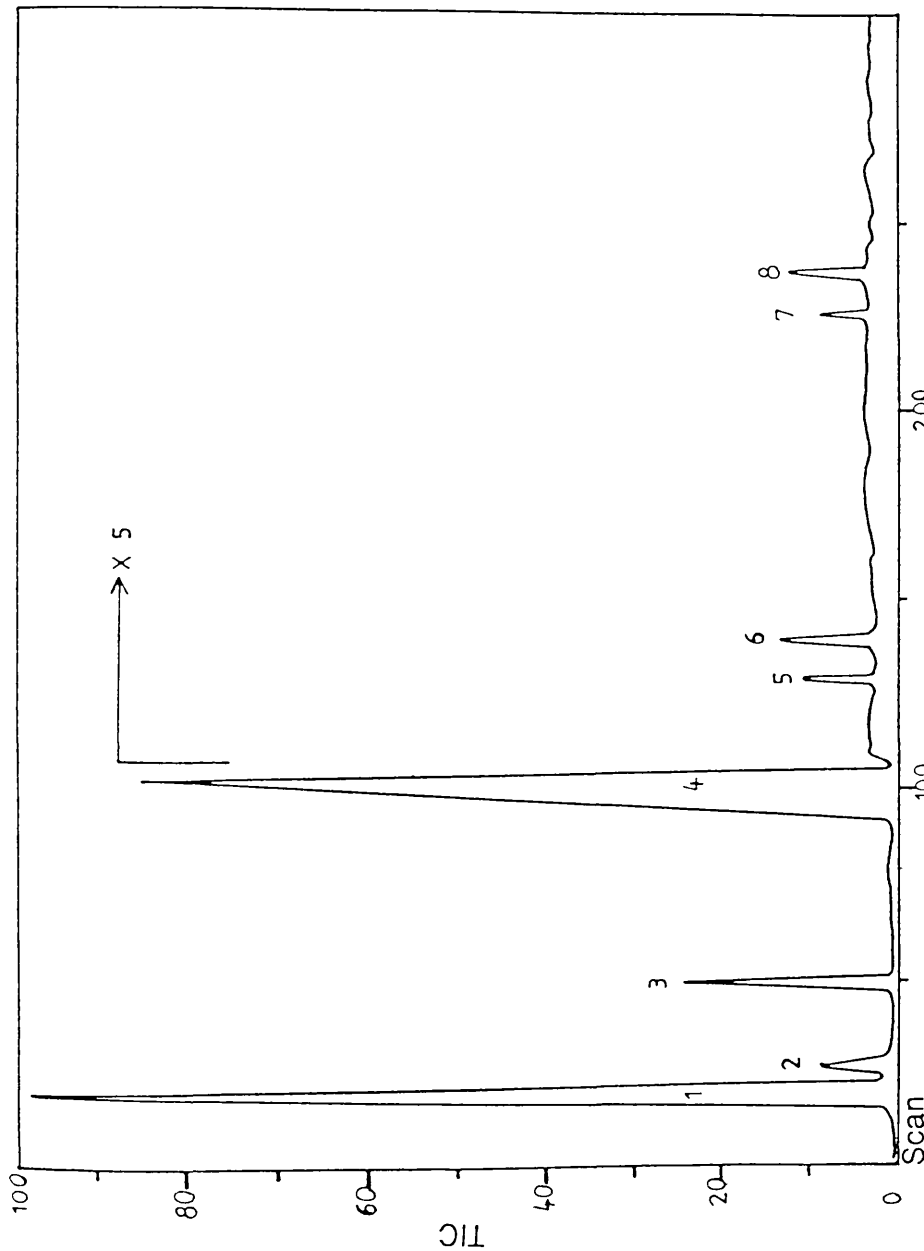


Fig. 5.6. GC data for the volatile liquid fraction from degradation of (PS12) in the TVA system under vacuum for 15 min at 300 °C.

Assignments: 1; Diethylether, 2; Benzene, 3; Toluene, 4; Styrene, 5; Allylbenzene, 6; α-methylstyrene 7; 1-methylindene, 8; Naphthalene.

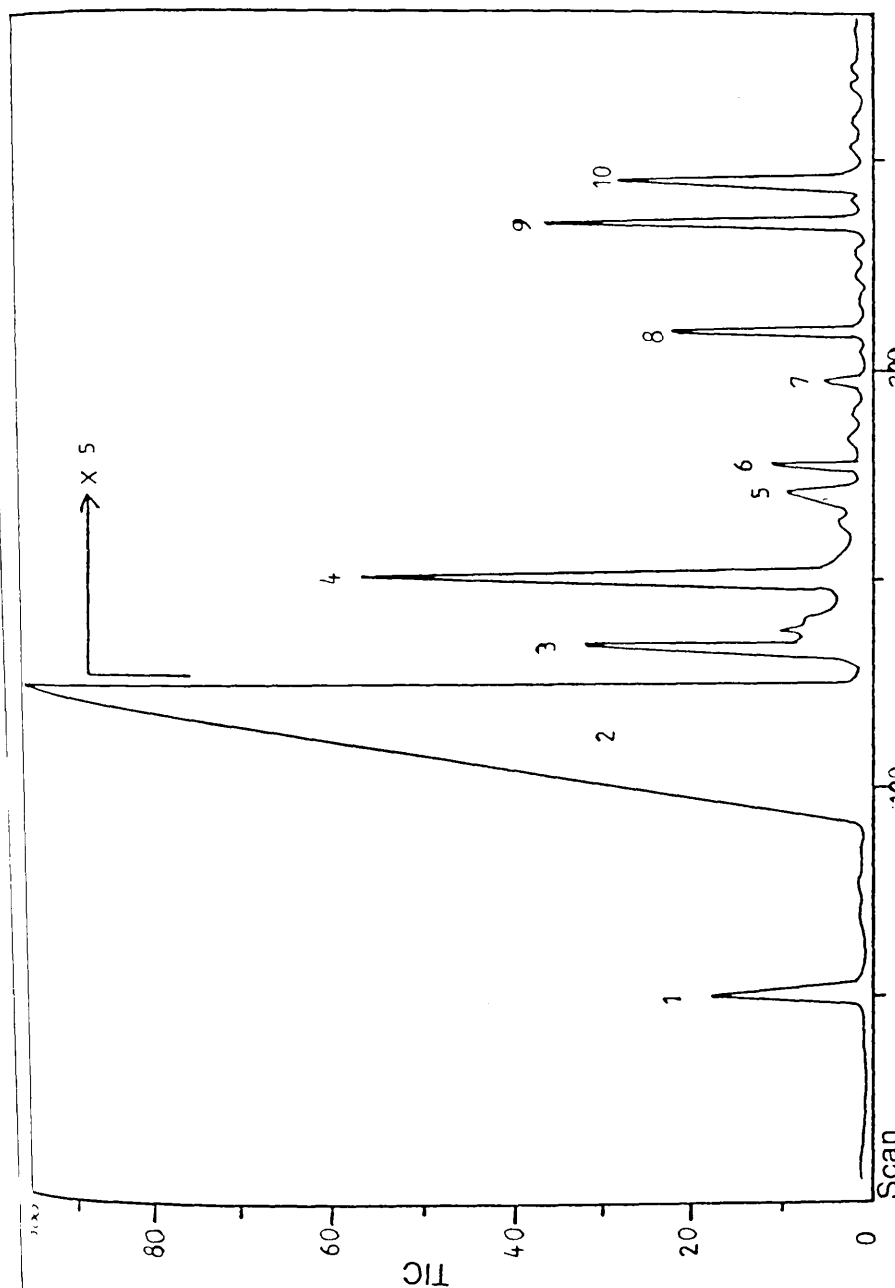


Fig. 5.7. GC data for the volatile liquid fraction from degradation of (PS12) in the TVA system under vacuum for 15 min at 350 °C.

Assignments: 1; Toluene, 2; Styrene, 3; Allylbenzene,
4; ∝-methylstyrene, 5; Trans-2-methylstyrene,
6; 4-phenyl-1-butene, 7; 3-methylindane,
8; Dimethylindane, 9; 1-methylindene,
10; Naphthalene.

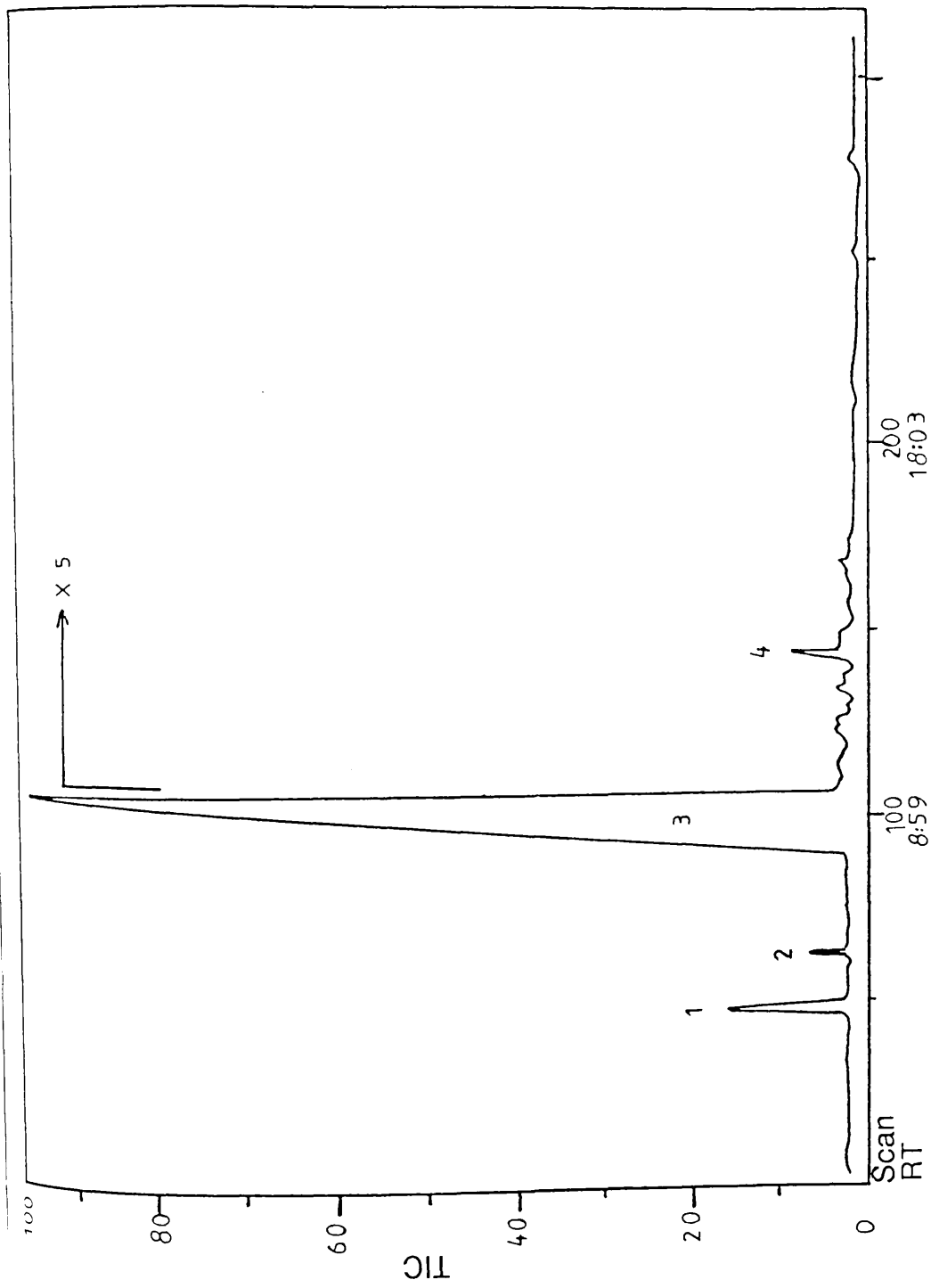


Fig. 5.8. GC data for the volatile liquid fraction from degradation of (PS12) in the TVA system under vacuum for 15 min at 420 °C. Assignments: 1; Toluene, 2; Ethylbenzene, 3; Styrene, 4; α-methylstyrene.

Table 5.4 Volatile Products in Degradation of PS12 at Several Temperatures, Listed in Order of Importance.

300 °C	350 °C	420 °C
Styrene	Styrene	Styrene
Toluene	Toluene	Toluene
Benzene	∝-Methylstyrene	Ethylbenzene
Naphthalene	1- Methylindene[a]	∝-Methylstyrene
∝-Methylstyrene	3-Phenylpropene[a]	
1-Methylindene[a]	Naphthalene	
3-Phenylpropene[a]	Dimethylindene[a]	
	Trans-2-methylstyrene	
	3-Methylindane[a]	
	4-Phenyl-1-butene[a]	

[a]Assignments based on comparison with fragmentation patterns in library mass spectra.

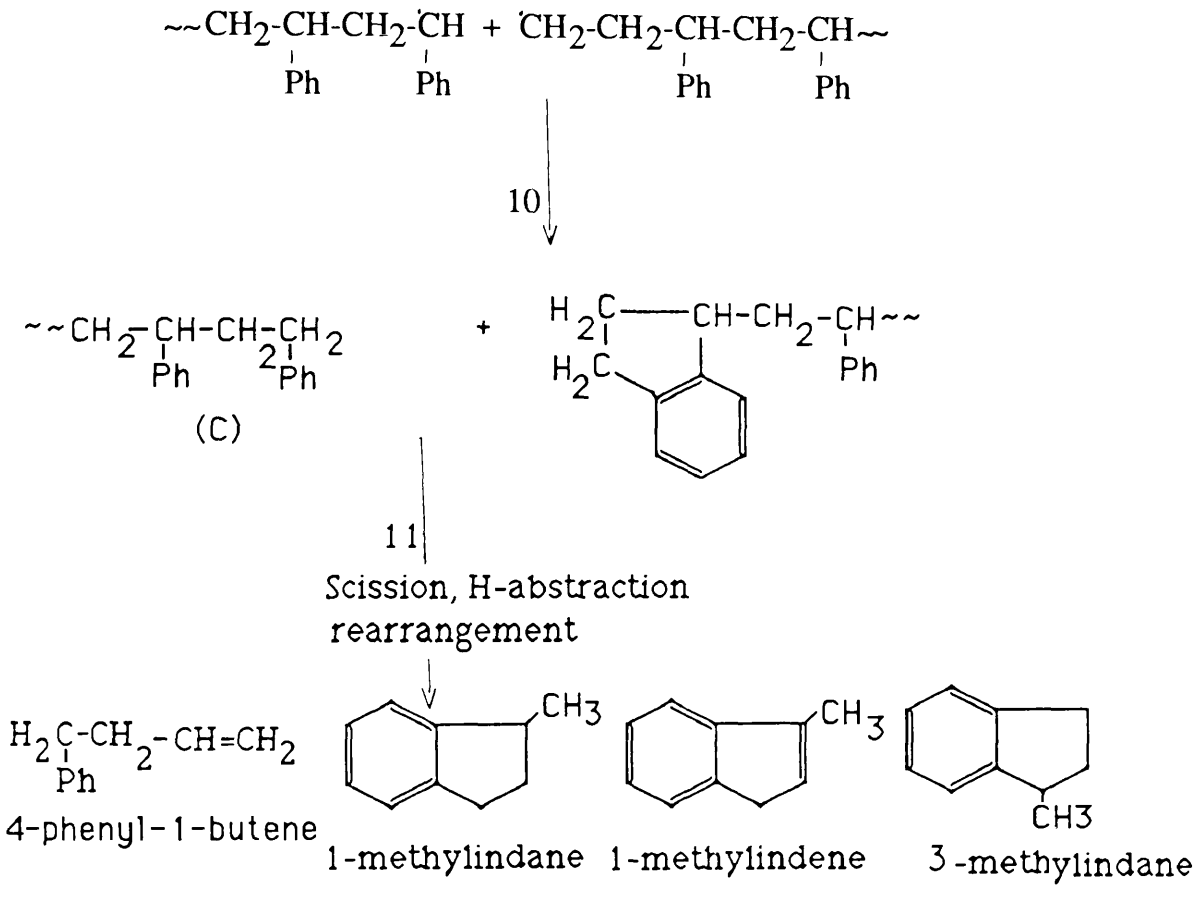
Benzene is present only in the products at 300 ^{o}C and naphthalene is found in small amounts at 300 ^{o}C and 350 ^{o}C. It is possible that the latter is present as an impurity in the polymer, although the polymer was subjected to several reprecipitations.

Toluene is produced at all temperatures, and this suggests that random scission of chains (reaction 1) occurs, as previously indicated. As it has already been noted, one of the possible sources ofα-methylstyrene is the vinylidene end structure (D). This can result either from random scission followed by disproportionation (reaction 2) or by scission of on-chain macroradicals (reaction 7b), following intermolecular transfer. The surge in formation of this product at 350 ^{o}C and its subsequent decline are consistent with the view of intermolecular transfer as a reaction which is important only in the earlier stages of degradation.

The presence of 1-Methylindene at 300 ^{o}C and 350 ^{o}C and the group of indene/indane type products and alkenes formed only at 350 ^{o}C, can be explained by decomposition related to the head to head linkages present in polystyrene made anionically using sodium naphthalenide. It has been suggested,[117] that these structures are thermally labile. The various products, with the exception of dimethylindene, can be accounted for by reactions 9-13.

Since several of the reaction products in this group can derive only from the head to head linkage, it was considered useful to carry out a similar investigation with a polystyrene sample made by the free radical route.

$$\sim CH_2\text{-}\underset{\displaystyle Ph}{CH}\text{-}CH_2\text{-}\underset{\displaystyle Ph}{CH}\text{-}CH_2\text{-}CH_2\text{-}\underset{\displaystyle Ph}{CH}\text{-}CH_2\text{-}\underset{\displaystyle Ph}{CH}\sim \xrightarrow{9}$$


10
(C)
11
Scission, H-abstraction
rearrangement
4-phenyl-1-butene
1-methylindane
1-methylindene
3-methylindane
Scission at a,
rearrangement
B +
2-methylstyrene
or
3-phenylpropene
12
(J)
13
Scission at b,
rearrangement
A +
4-phenyl-1-butene

Free radical polystyrene was degraded following the same procedure, isothermally at 300°, 350° and 420 °C under TVA conditions. The chromatogram for products of degradation of a 100 mg PS180 sample at 300 °C for 15 min is shown in Fig. 5.9. The same PS sample was then heated successively for 15 min at 350 °C and 15 min at 420 °C and the corresponding chromatograms are shown in Figs. 5.10 and 5.11, respectively. The data indicate the expected products styrene, toluene and ∝-methylstyrene. In Fig. 5.9 the presence of the initiator end fragment as 2-cyanopropane is also indicated, showing that end initiation from these ends readily occurs. The minor products of reactions 9-13 are barely detectable, only at 350 °C, as would be expected from the low concentration of head to head linkages resulting in the termination step of the free radical polymerisation.

Benzene appears to be a genuine product of degradation at 300 °C from both PS12 and PS618; but it is not formed at the higher temperatures used. Ethylbenzene is produced only from PS12 at 420 °C and is not detected at 300 °C or 350 °C.

2.5.2. Cold Ring Fraction

The cold ring fraction of products volatile under vacuum at degradation temperature but not at ambient temperature, obtained by heating 150 mg of the polymer at 10 °C/min to 500 °C, was separated and analysed by GC-MS. Each polymer gave similar results, indicating four main products. A typical chromatogram is illustrated in Fig. 5.12. The two major products are the dimer (K) and trimer (L) as already mentioned in Chapter Four. These are the products expected by intramolecular transfer of radical (A): dimer (K) results from reaction 6 as written and trimer (L) by corresponding H-abstraction at the next tertiary site along the backbone.

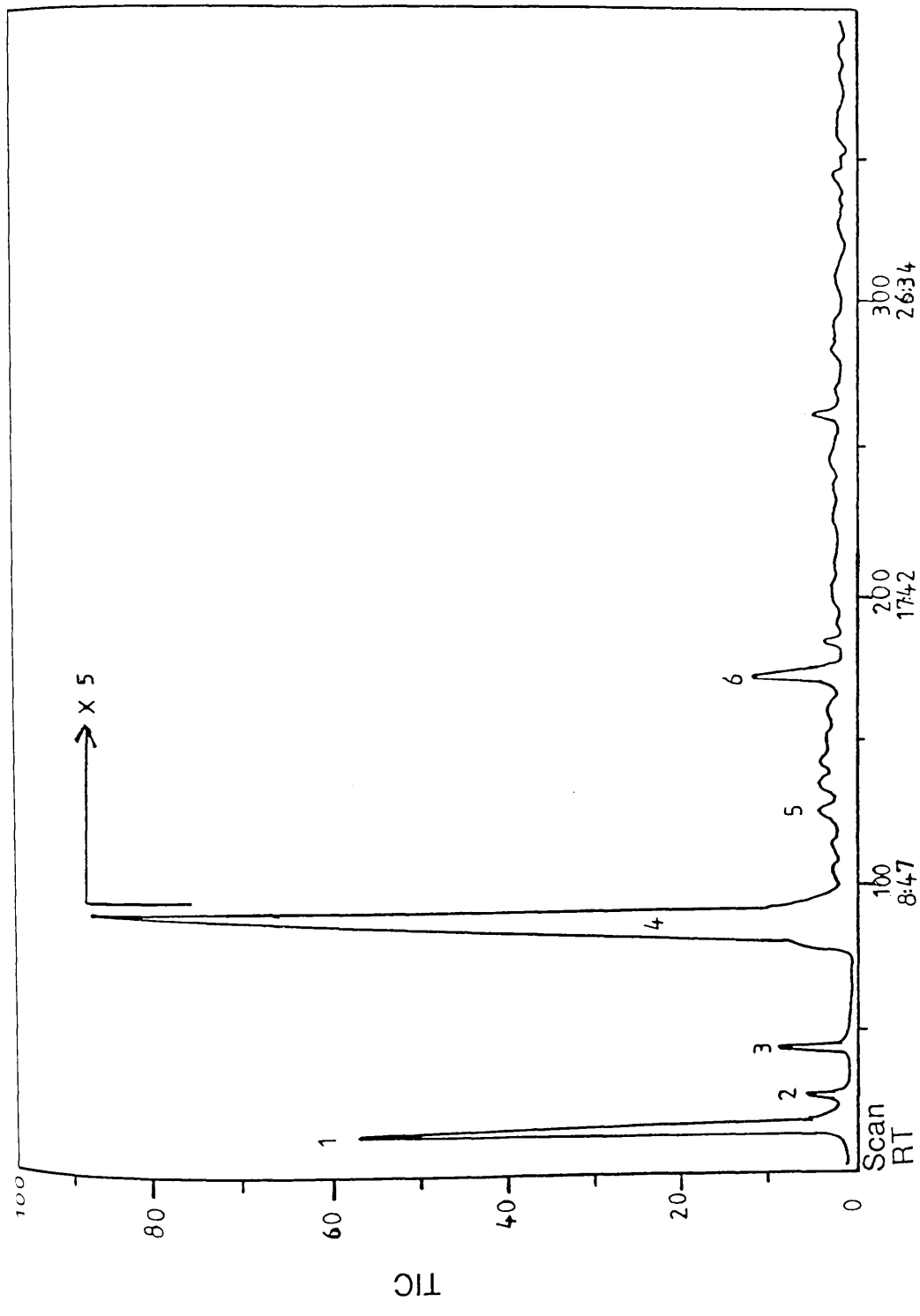


Fig. 5.9. GC data for the volatile liquid fraction from degradation of (PS180) in the TVA system under vacuum for 15 min at 300 °C.

Assignments: 1; Solvent, 2; Benzene, 3; Toluene, 4; Styrene, 5; α-methylstyrene, 6; 2-cyanopropane.

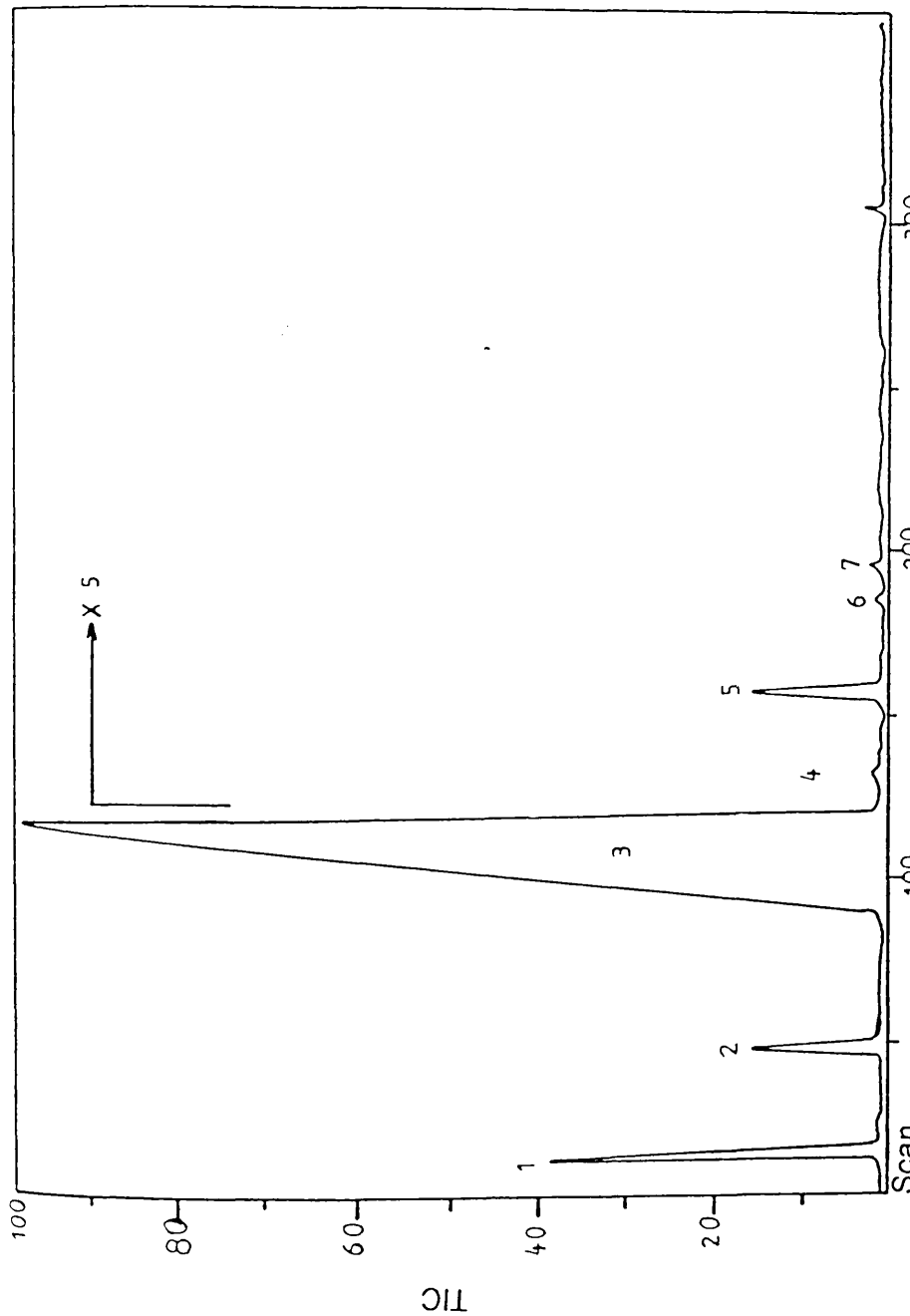


Fig. 5.10. GC data for the volatile liquid fraction from degradation of (PS180) in the TVA system under vacuum for 15 min at 350 °C.

Assignments; 1; Solvent, 2; Toluene, 3; Styrene, 4; Allylbenzene, 5; α-methylstyrene, 6; Trans-2-methylstyrene, 7; 1-methylindene.

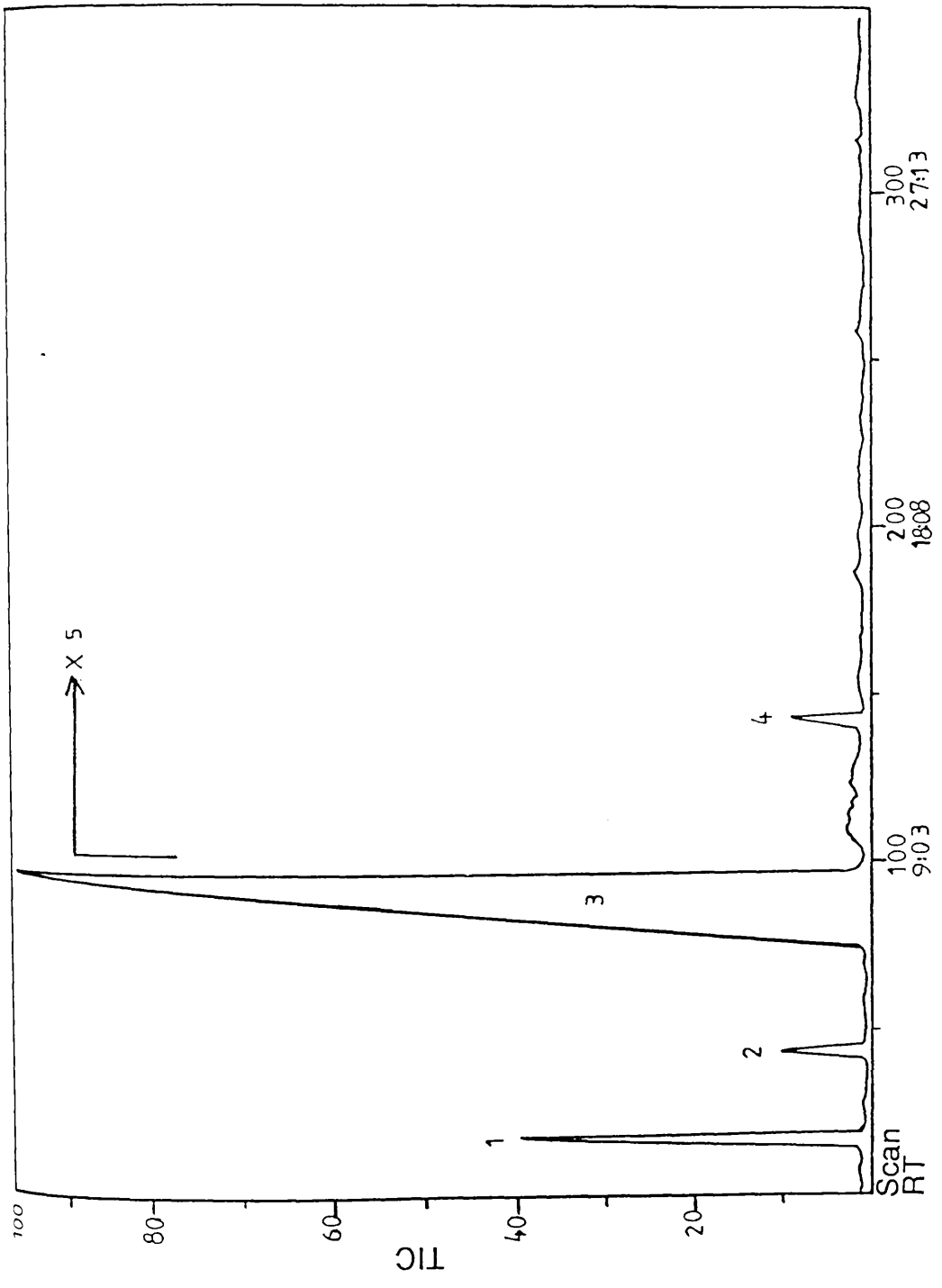
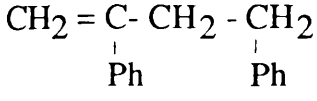
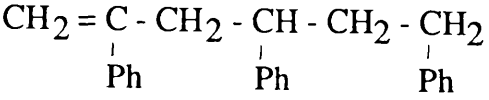


Fig. 5.11. GC data for the volatile liquid fraction from degradation of (PS180) in the TVA system under vacuum for 15 min at 420 ^{o}C. Assignments: 1; Solvent, 2; Toluene, 3; Styrene, 4; α-methylstyrene.

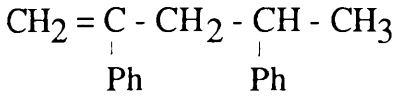


(K)

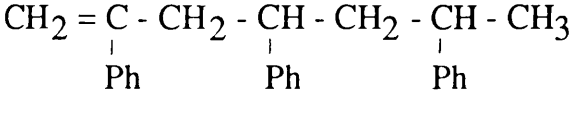


(L)

Less important, but still significant, are the corresponding products with an extra methyl group, (M) and (N):

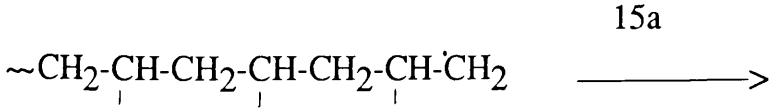


(M)

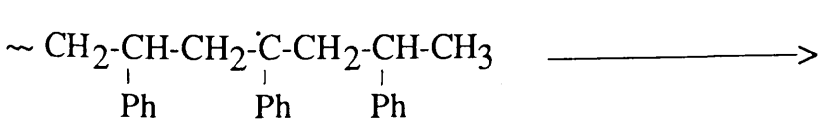


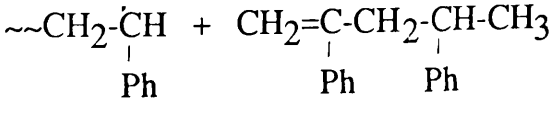
(N)

These can be produced by intramolecular reaction of radical (B). The reaction leading to the "dimer" is shown as reaction 15:



(B)





(A) (M)

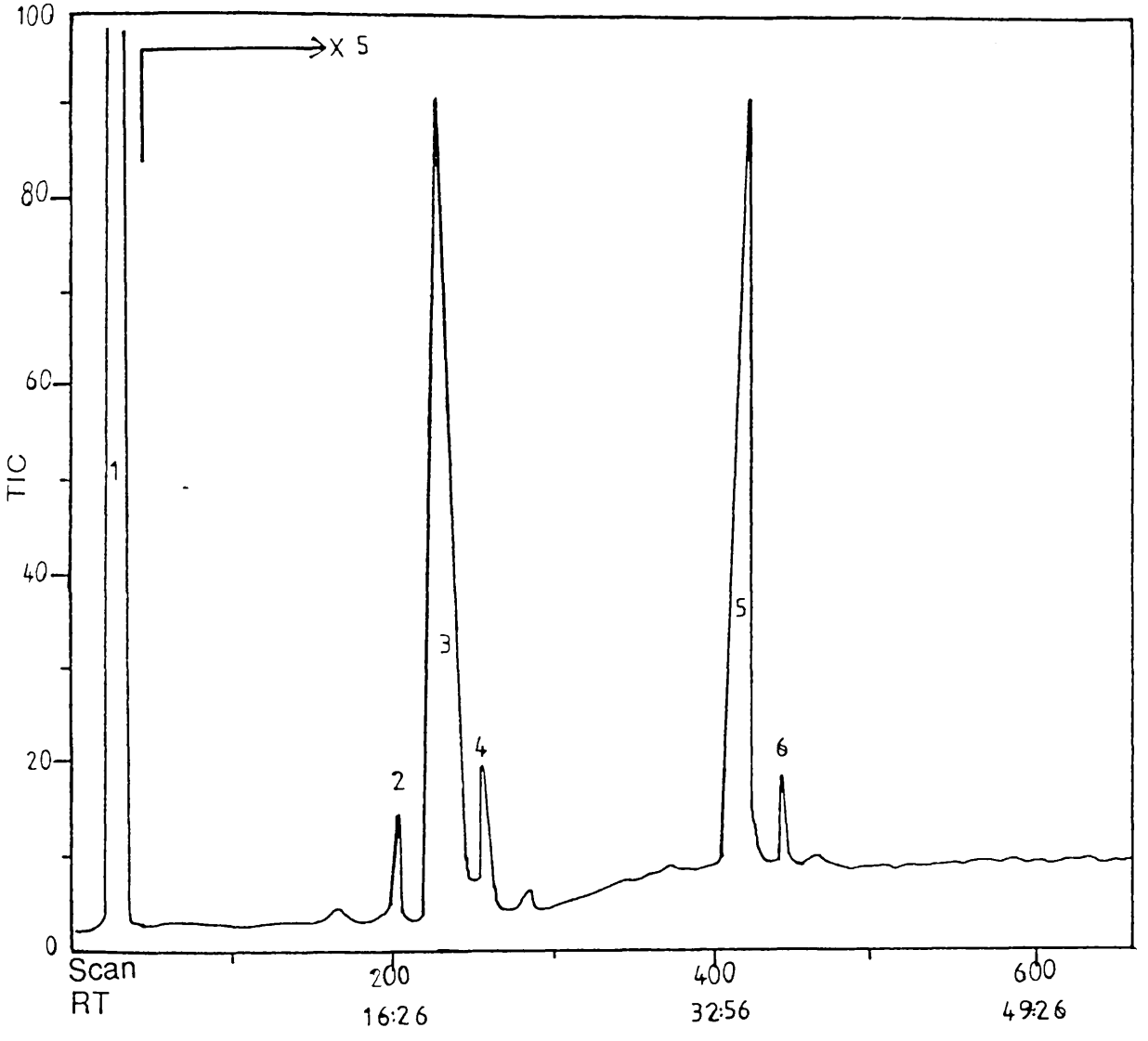


Fig. 5.12. GC data for the cold ring fraction from degradation of (PS12) in the TVA system under vacuum at 10 ^{o}C/min to 500 ^{o}C.

Assignments: 1; Solvent, 2; 1,3-diphenylpropane, 3; 2,4-diphenyl-1-butene, 4; 2,4-diphenyl-1-pentene, 5; 2,4,6-triphenyl-1-hexene, 6; 2,4,6,-triphenyl-1-heptene.

and the corresponding "trimer" is formed by similar intramolecular H-abstraction at next tertiary hydrogen site along the backbone.

The reaction of radical (B) to give the CRF products (M) and (N), with consequent formation of radical (A), may be compared with the analogous process leading to radical (A), and∝-methylstyrene. The formation of significant amounts of these CRF products (compared with the amount of ∝-methylstyrene) provides a possible explanation for the imbalance in the yields of toluene and ∝-methylstyrene referred to above.

3. CONCLUSIONS

This study confirms the view that most of the volatile liquid formation in polystyrene degradation depends on reactions of the secondary macroradical formed by backbone scission. The same radical is also responsible for generation of the major proportion of CRF products.

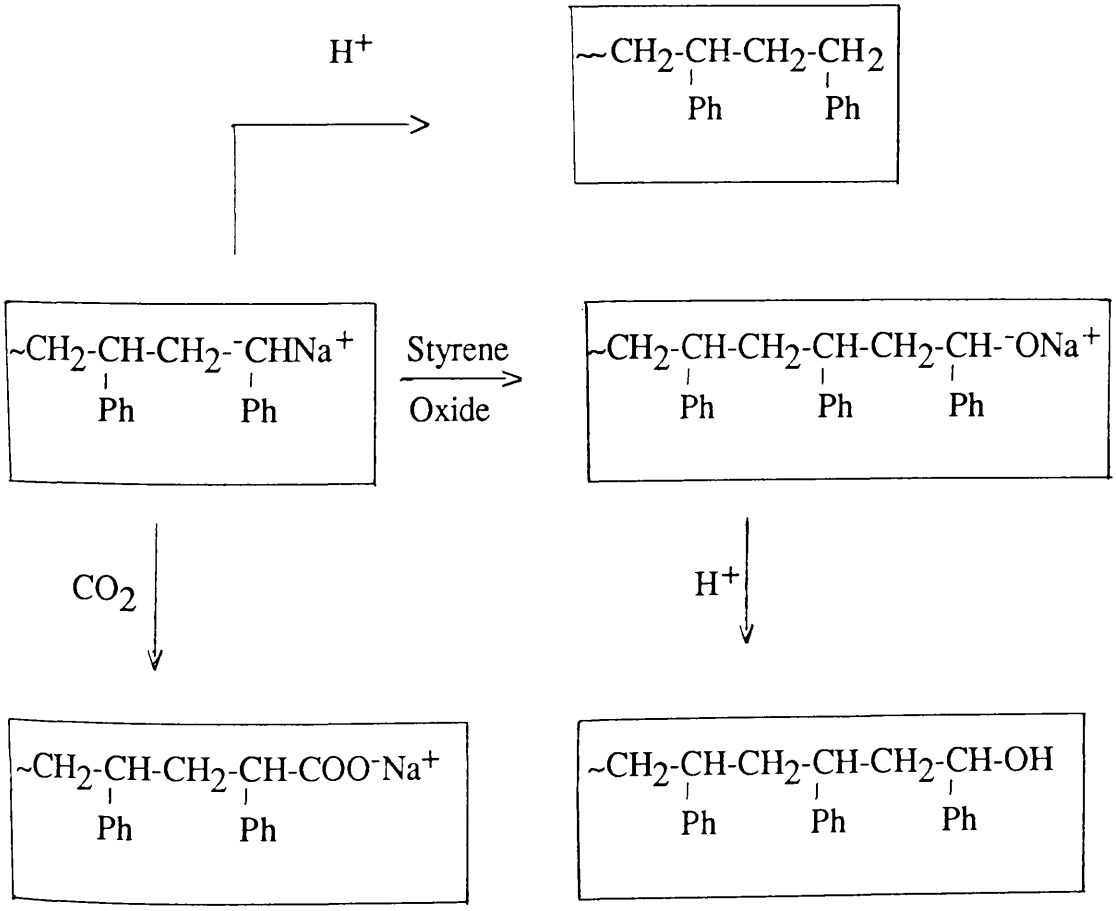
The primary macroradical in polystyrene degradation is seen as interconverting to the secondary macroradical with release of∝-methylstyrene or a 5 or 7-backbone carbon CRF product by intramolecular transfer, or reacting by intermolecular transfer in the earlier stages of volatilisation. The results of this investigation show clearly that the volatile liquid to CRF ratio is not constant over the total range of extent of degradation. In the first 30% of reaction, during which the rapid fall in molecular weight is occurring, the ratio changes rapidly, but therafter (i.e. once the molecular weight has stabilised at about $\bar{M}n$ 5000) it remains approximately constant at a particular degradation temperature.

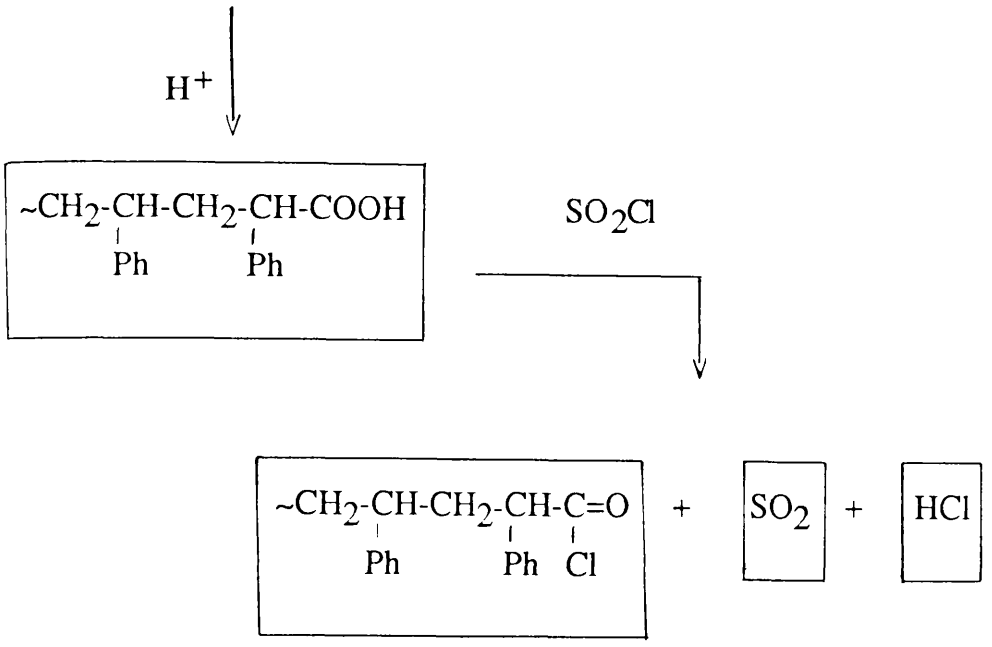
Several minor products of degradation can be traced to the head to head structures present in sodium naphthalenide initiated polystyrene.

CHAPTER SIX

FUNCTIONALLY-TERMINATED POLYSTYRENE

Thermal degradation of low molecular weight polystyrenes containing various chain ends such as hydroxyl, carboxyl and acid chloride has been studied and thermal decomposition mechanisms have been elucidated. The volatile products were separated by the SATVA technique and analysed by IR, MS, GC and GC-MS. The polymers with different chain ends were obtained from living polystyrene.





1. INTRODUCTION

Polymerisation proceeding without any termination has been known for a long time.[45] The lack of termination which is characteristic of "living" polymers permits synthesis of polymers possessing specific end groups. Polymerisation proceeds without termination and the reactive ends of living polymers may be killed by introducing a suitable reagent.

In the present studies, acidified methanol was introduced to place a hydrogen atom on the end of the polymer chain. Similarly styrene oxide and carbon dioxide were introduced to terminate the chains with hydroxyl and carboxyl groups. Other reagents of this type include addition of carbon disulphide, which gives a thiocarboxyl group on the end of the polymer chain.[83,91,92] Rempp and Loucheux[88] obtained carboxyl-terminated polystyrene by reacting the carbanion ends with succinic or phthalic anhydride. Similarly, Meyer et al.[89] terminated polystyrene carbanion ends with p-aminoethylbenzoate.

These reactions are particularly useful if a polymer with two "living" ends is formed, since the bifunctional polymer may then be used in coupling reactions,

for example to synthesise block co-polymers.[84,90,91] In the present studies, such polymers have been reacted with 1,6-diaminohexane and 2,2-dihydroxyl-4,4-dimethoxybenzophenone.

A problem which is deserving of investigation is the effect of end groups on polymer properties, particularly the thermal stability. A batch of polystyrenes of comparable molecular weight, prepared by anionic polymerisation as described in Chapter Three, were end-capped with various structures. By using this method of preparation, it was found that polymers possessing $-COO^-Na^+$ end groups are considerably more associated (greater viscosity in solution) than those with $-CHNa^+$ end groups and a still greater degree of association characterised polymers having $-CH_2O^-Na+$ ends. This effect has also been observed by Brody and co-workers.[90] Polymers which were used for the present studies have very low closely similar molecular weights (5000-6228) to avoid the possible effects of the concentration of chain ends. The polymers used in this investigation are listed in Table 6.1.

1.2. Degradation Behaviour of Normal Polystyrene

The thermal degradation of anionically prepared polystyrenes, with benzylic chain ends, discussed in Chapter Five, provides the basis for comparison of the effect of terminal functional groups on the stability, product composition and degradation mechanism, considered in this Chapter.

2. PROGRAMMED HEATING EXPERIMENTS

2.1. THERMOGRAVIMETRY

The TG and DTG curves for the hydroxyl, carboxyl and acid chloride-terminated polystyrene samples were obtained under dynamic nitrogen at a heating rate of

10°C/min. The curves for the three polymers are illustrated in Figs. 6.1, 6.2 and 6.3.

Figs. 6.1 and 6.2 show a single rate maximum which confirms the single step nature of the volatilisation process. The hydroxyl and carboxyl-terminated polystyrenes begin to lose weight at 327 °C and 325 °C and about 50% weight loss occurred at 398 °C and 370 °C, respectively.

The DTG curves show T_{max} at 414 °C and 408 °C, respectively. The TG and DTG curves for the acid chloride-terminated polymer are shown in Fig. 6.3. The initial weight loss which starts at approximately 200 °C and achieves a rate maximum at 230 °C is probably due to evolution of HCl. The second stage, which is the main stage of decomposition of the polymer, starts near 300 °C and about 50% weight loss has occurred at about 380 °C. It is evident that initial weight loss begins at a lower temperature in acid chloride-terminated polystyrene than is observed for the hydroxyl and carboxyl-terminated polymers. Weight loss reaches 50%, however, at a higher temperature than in the case of carboxyl-terminated polystyrene and at a lower temperature than of hydroxyl-terminated polystyrene.

2.2. DIFFERENTIAL THERMAL ANALYSIS

DTA curves for the hydroxyl, carboxyl and acid chloride-terminated polystyrene samples were obtained under dynamic nitrogen at a heating rate of 10 °C/min and are virtually identical to that for normal polystyrene. The curves are reproduced in Fig. 6.4. Each DTA curve shows a single broad peak which confirms the endothermic nature of the bond scission process. The main features of the thermal behaviour, established by DTA, TG and DTG, are summarised in Table 6.2.

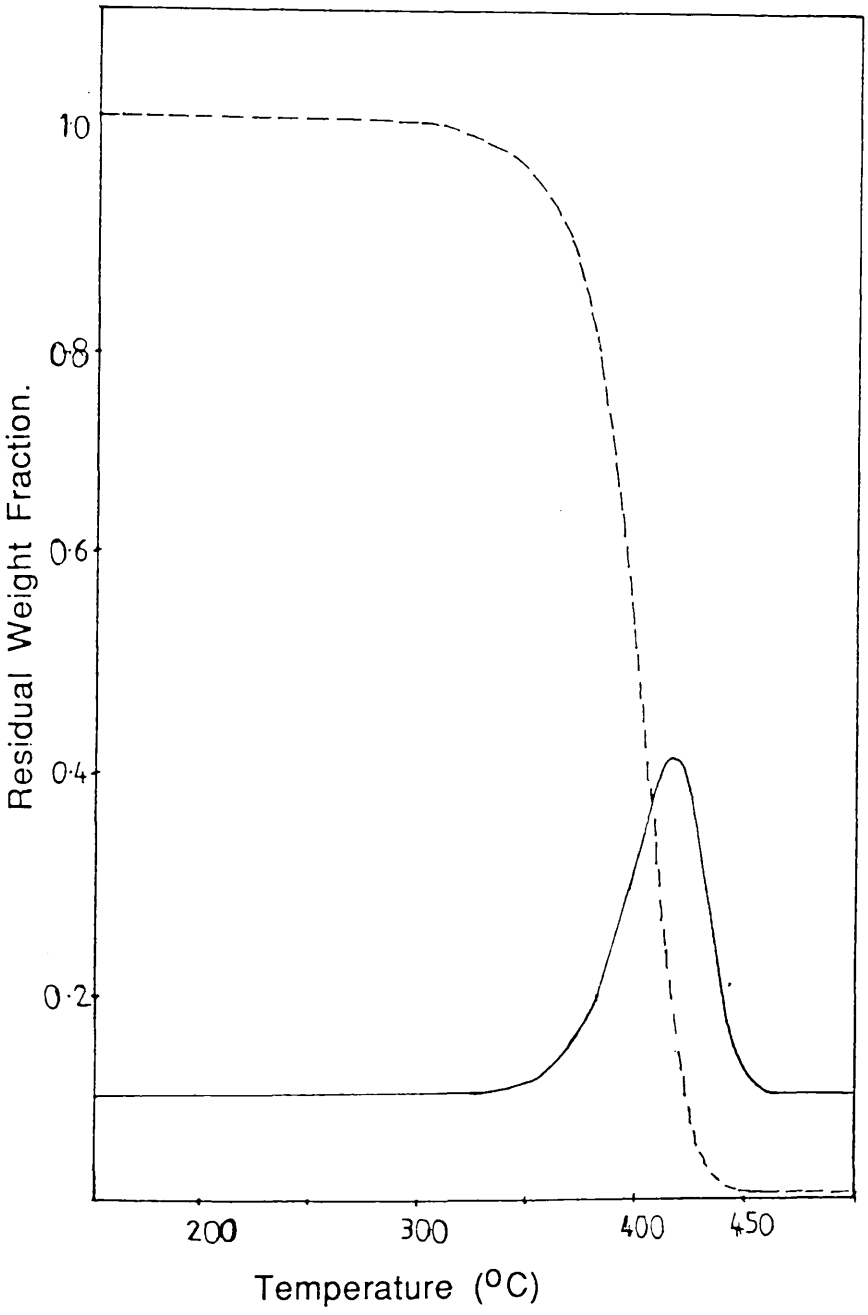


Fig. 6.1. TG and DTG curves for HO-PS-OH.

Keys: _ _ _ TG, ___ DTG

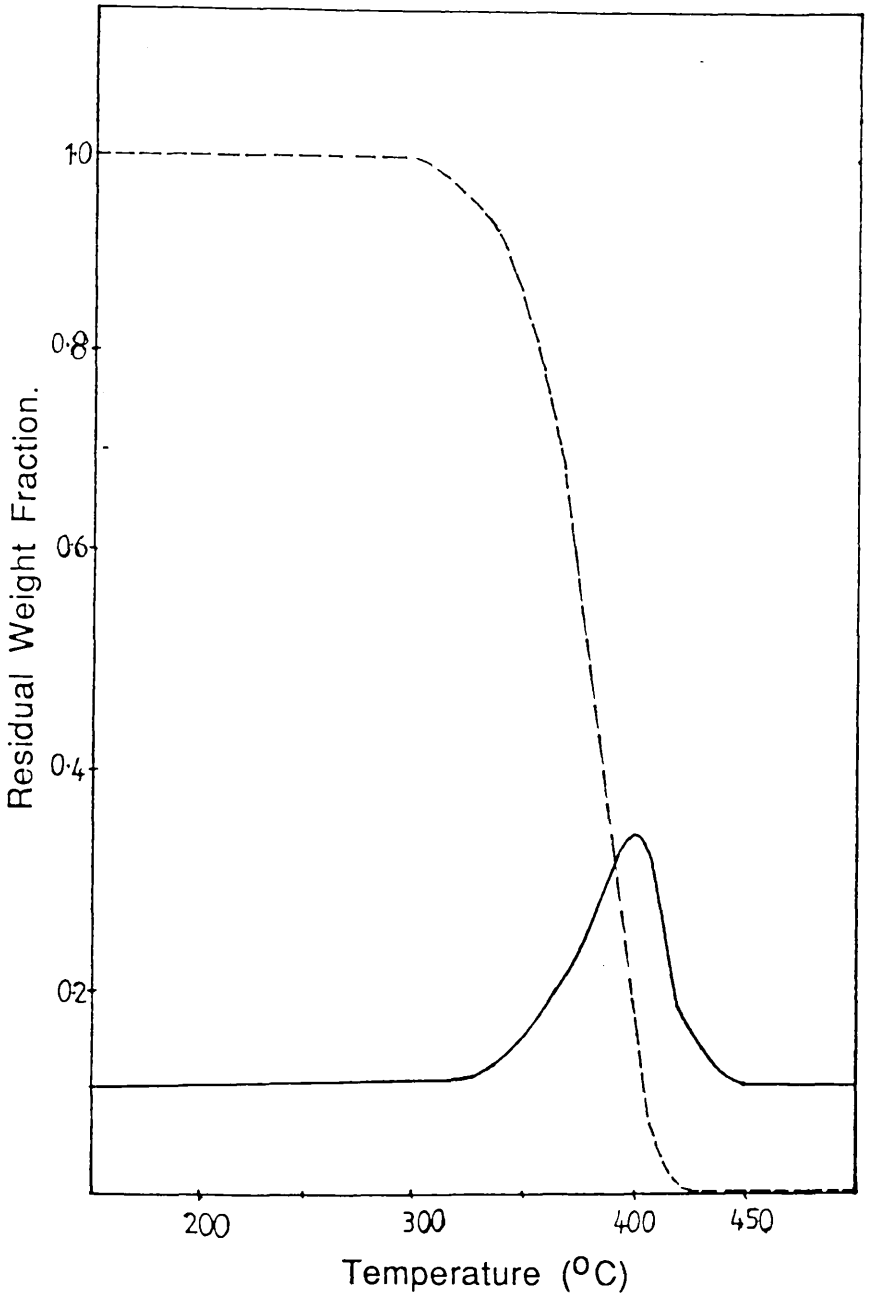


Fig. 6.2. TG and DTG curves for HO_2C-PS-CO_2H.

Keys: - - - TG, ___ DTG.

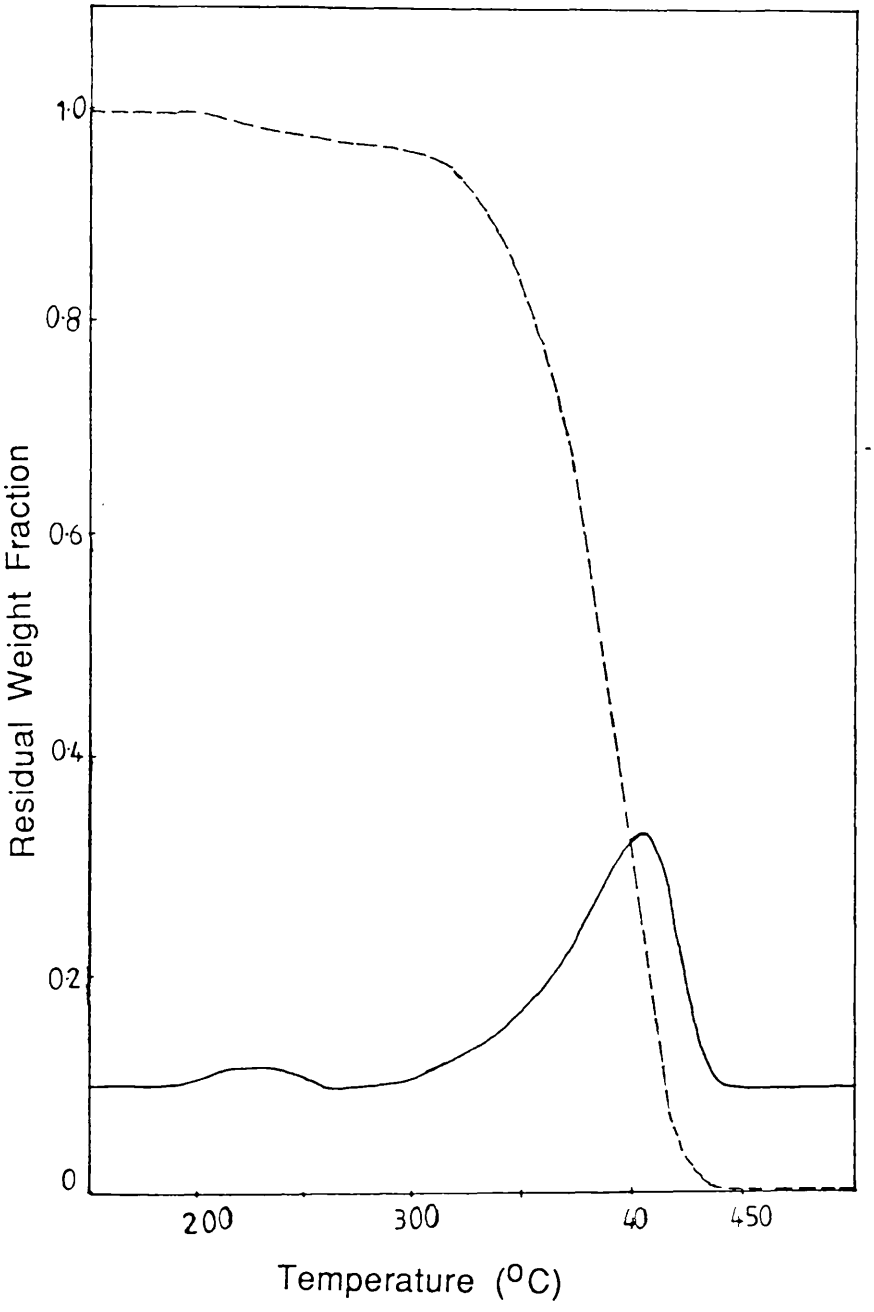


Fig. 6.3. TG and DTG curves for ClOC-PS-COCl.
Keys: _ _ _ TG, ___ DTG.

Table 6.1 Functionally-Terminated Polystyrene Samples

Sample	Type	$\bar{M}n$	$\bar{M}w/\bar{M}n$
PS	Anionic	5,000	1.3
HO-PS-OH	Anionic	6,228	1.5
HO_2C-PS-CO_2H	Anionic	5,532	1.6
ClOC-PS-COCl	Anionic	5,600	1.6

Table 6.2 DTA,TG and DTG Data for Functionally-Terminated Polystyrene Samples.

	DTG		TG		DTA	
Polymer	Peak temp., °C	Temp. range, °C	1% Wt. loss at °C	50% wt.loss at °C	Peak temp., °C	Temp. range, °C
HO-PS-OH	414	327-450	327	398	422	350-450
HO_2C-PS-CO_2H	408	325-450	325	370	416	325-445
ClOC-PS-COCl (200-250°C)	410	300-450	225	380	420	325-450

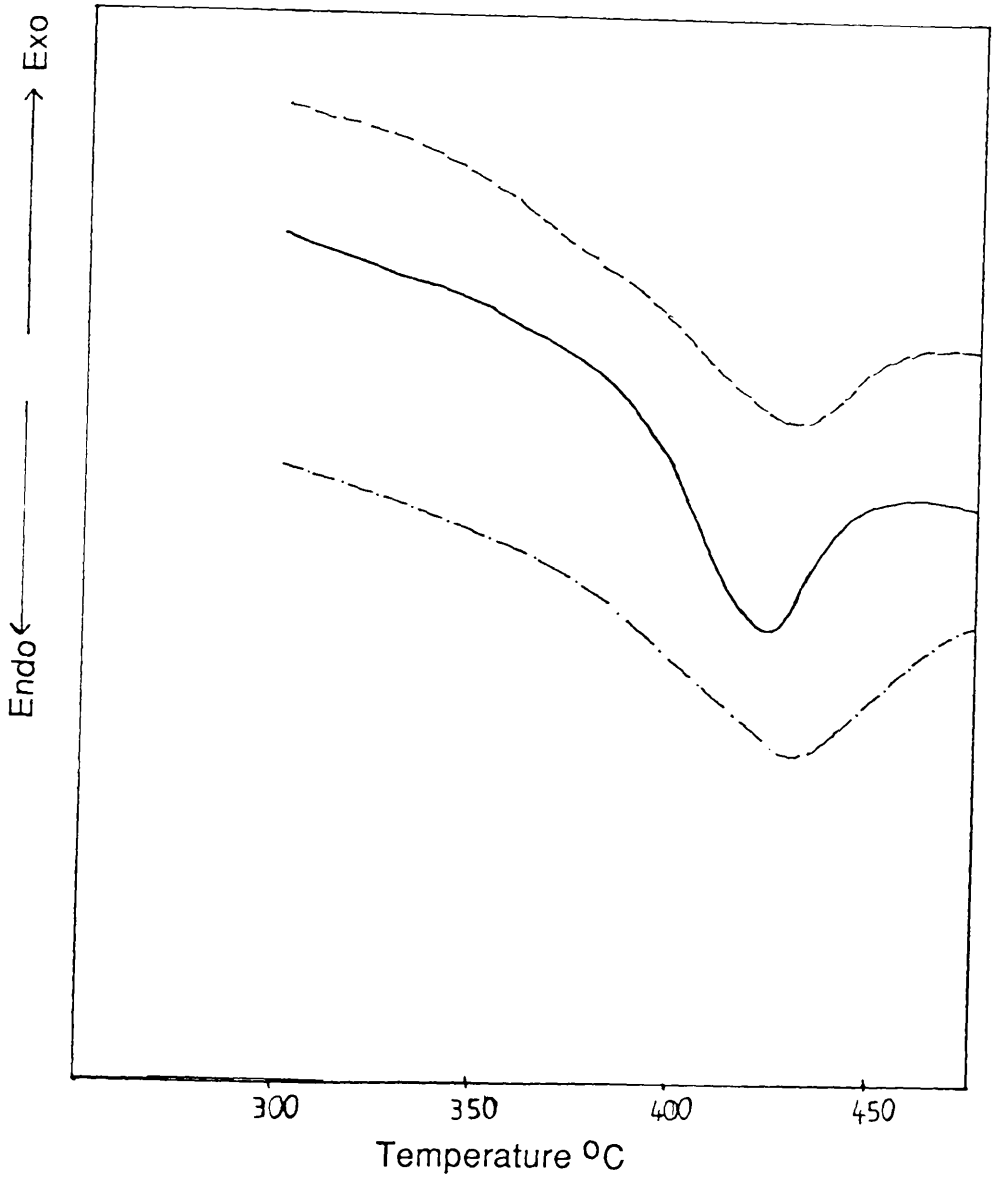


Fig. 6.4. DTA curves for functionally-terminated Polystyrenes (Nitrogen, 10 °C/min).

Keys: ___HO-PS-OH, _ _ HO_2C-PS-CO_2H, _ _ _ _ ClOC-PS COCl.

2.3. THERMAL VOLATILISATION ANALYSIS

The polystyrene samples with hydroxyl, carboxyl and acid chloride end groups were examined as 40 mg powder samples in a TVA system under vacuum using programmed heating at a rate of 10 ^{o}C/min to 500 ^{o}C. The TVA curves for these three polymers are shown in Fig. 6.5(a,b,c).

Figs. 6.5a and 6.5b show a single stage decomposition as for normal polystyrene but it is evident from the separation of the traces that the product composition is different in each case. Fig. 6.5b shows more separation between the TVA traces for 0 ^{o}, -45 ^{o}, -75 ^{o} ,-100^{o} and -196 ^{o}C trap temperatures as the degradation temperature rises which indicates that a variety of products with different volatility are evolved at higher temperatures in the case of carboxyl-terminated polystyrene but not in the case of hydroxyl-terminated polystyrene (Fig. 6.5a). It is also clear from the TVA curves that the -196 ^{o}C trace remain on the base line in hydroxyl-terminated polystyrene but in the carboxyl-terminated polystyrene -196^{o}C moves near to -100 ^{o}C. This indicates that non-condensable gaseous products are evolved in the latter case, but not in the former.

Fig. 6.5c shows a two stage decomposition and from inspection of the separation of the TVA traces, it is evident that the product composition is different at each stage. The first stage, extending from 180 ^{o}C to 245 ^{o}C with T_{max} at 230 ^{o}C, could be due to dehydrochlorination, carbon dioxide and.a trace amount of carbonyl sulphide (O=C=S). The second stage of decomposition of acid chloride polymer is the main decomposition as for normal polystyrene. The amount of non-condensable gaseous products evolved in the second stage of decomposition is negligible.

The TVA data for these polymers are summarised in Table 6.3. On the basis of TVA, it is clear that there is no major difference in thermal behaviour in these

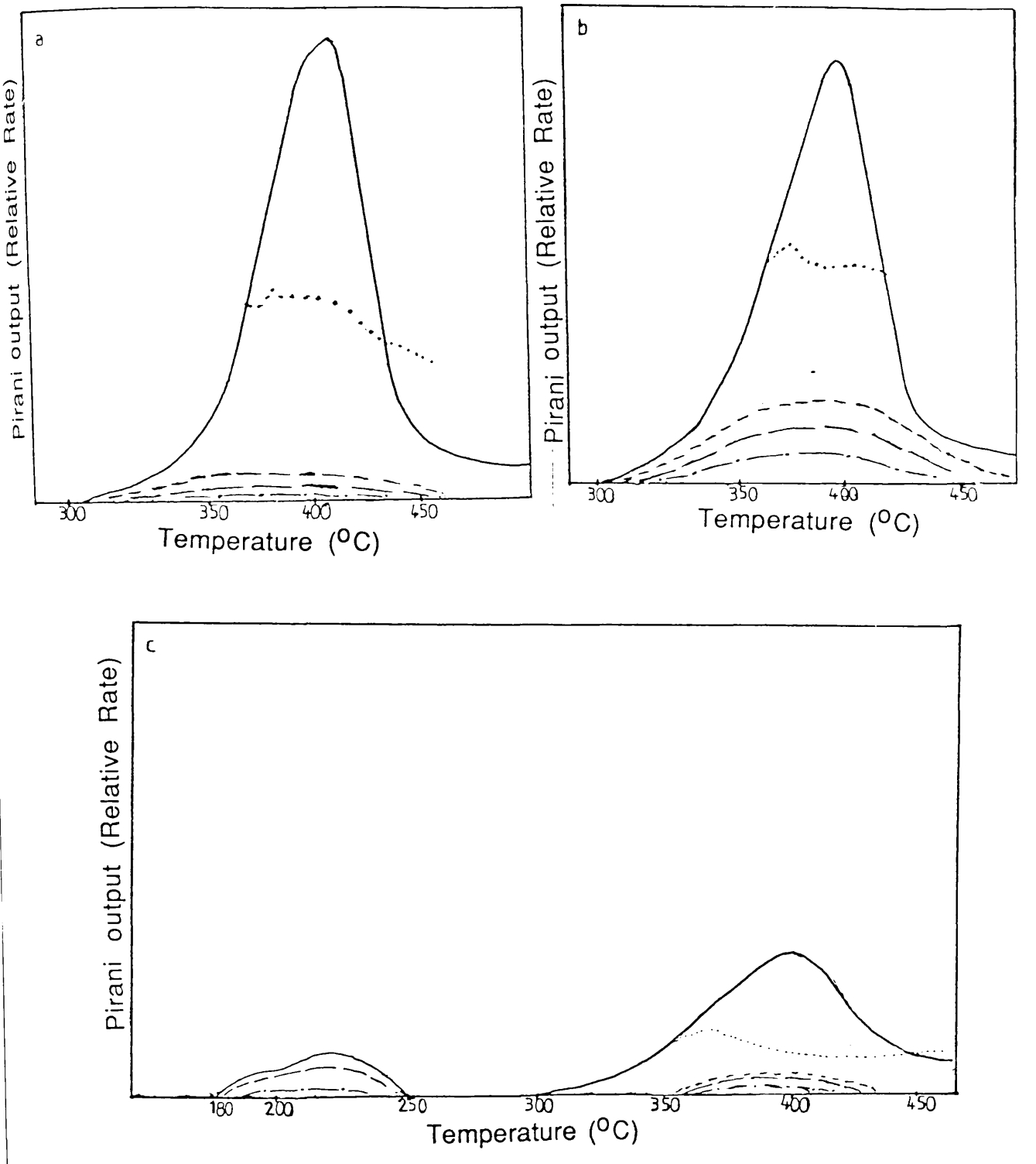


Fig. 6.5. TVA curves (vacuum, heating rate 10 °C/min) for functionally terminated Polystyrene to 500 °C.

(a) HO-PS-OH, (b) HO_2C-PS-CO_2H, (c) ClOC-PS-COCl.

Keys: ___ 0°, ... -45°, - - -75°, __ __ -100°, __ . __ -196 °C

polymer samples. In all three, the main decomposition begins above 300 ^{o}C. All the TVA curves show the limiting rate effect at -45 ^{o}C typical of styrene as the main volatile product, as already reported in Chapter Four for normal polystyrene.

2.3.1. Subambient Thermal Volatilisation

Condensable volatile degradation products were separated by the SATVA method. The SATVA traces for hydroxyl, carboxyl and acid chloride- terminated polystyrenes are shown in Figs. 6.6, 6.7 and 6.8, respectively. Products corresponding to each SATVA peak were collected separately for identification.

2.3.2. Product Analysis

The various degradation products, namely cold ring fraction, liquid fraction and gaseous products including non-condensable gases were examined after degradation of 60 mg of each polymer samples to 500 ^{o}C under TVA conditions. The degradation products were examined by IR, MS, ^{1}H-NMR and GC-MS techniques.

2.3.2.1. Residue

There was no significant amount of involatile fraction left in these experiments.

2.3.2.2. Cold Ring Fraction

The CRF materials were separated by thin layer chromatography and examined by infrared spectroscopy and mass spectrometry. These were light yellow materials with rather similar IR spectra, to the CRF from degradation of normal polystyrene, differing only in the absorption at 1705-1695 cm^{-1} due to carboxyl and carbonyl groups. The IR spectrum of the cold ring fraction of carboxyl-

Table 6.3 TVA Data for Degradation of PS, HO-PS-OH, HO_2C-PS-CO_2H and ClOC-PS-COCl Under Normal TVA Conditions to 500 °C.

Polymer	Initial temp. (T_i) °C	T_{max} °C	Wt% of condens-able volatile products at~500 °C	Wt% of cold ring fraction
PS	310	412	68	31.5
HO-PS-OH	311	410	65	32.25
HO_2C-PS-CO_2H	308	400	59	37.50
ClOC-PS-COCl (180°-245 °C)	306	408	62	35.0

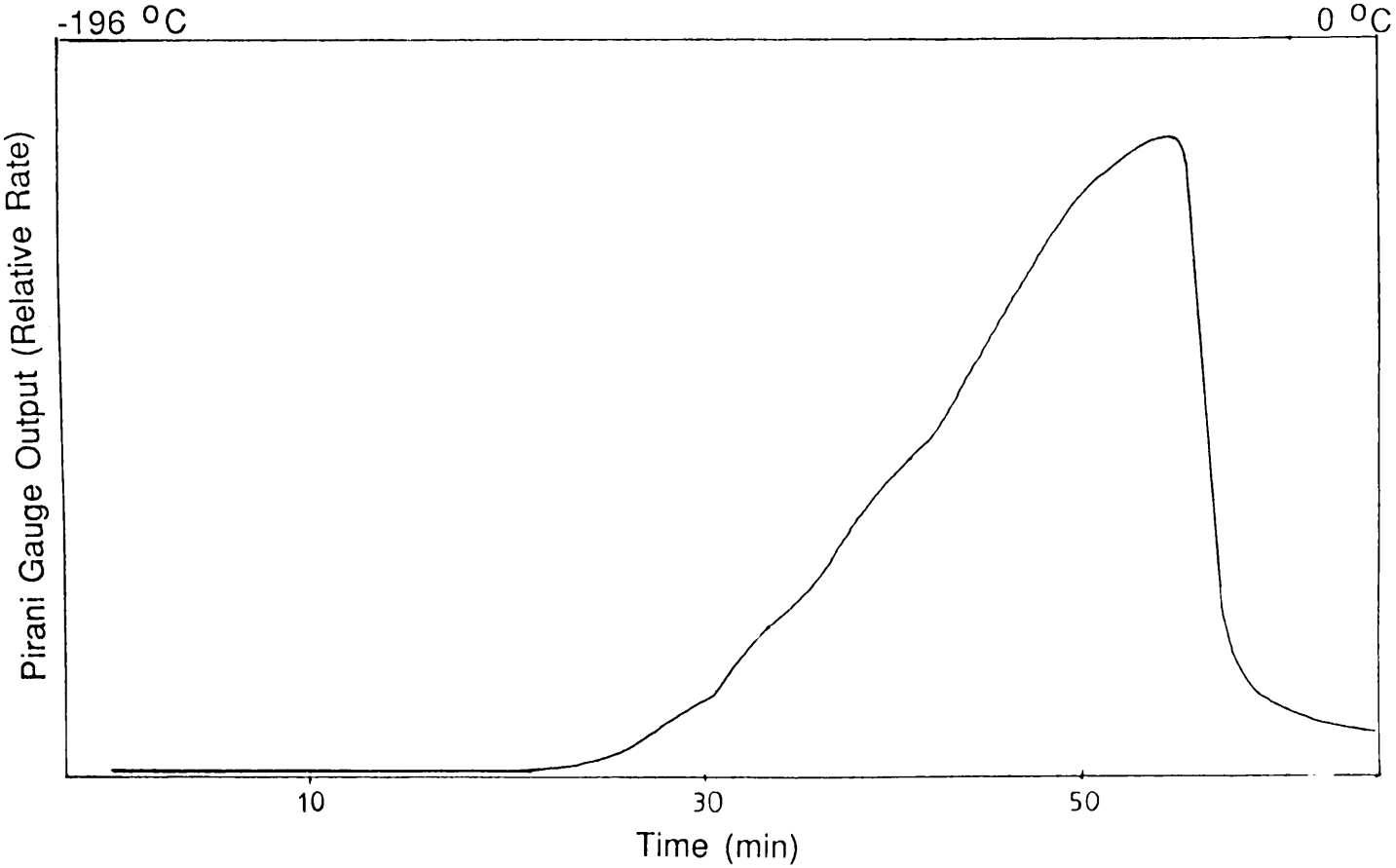


Fig. 6.6. SATVA curve for warm-up from -196 °C to 0 °C of condensable volatile product fraction from degradation to 500 °C under normal TVA conditions of dihydroxyl-terminated Polystyrene.

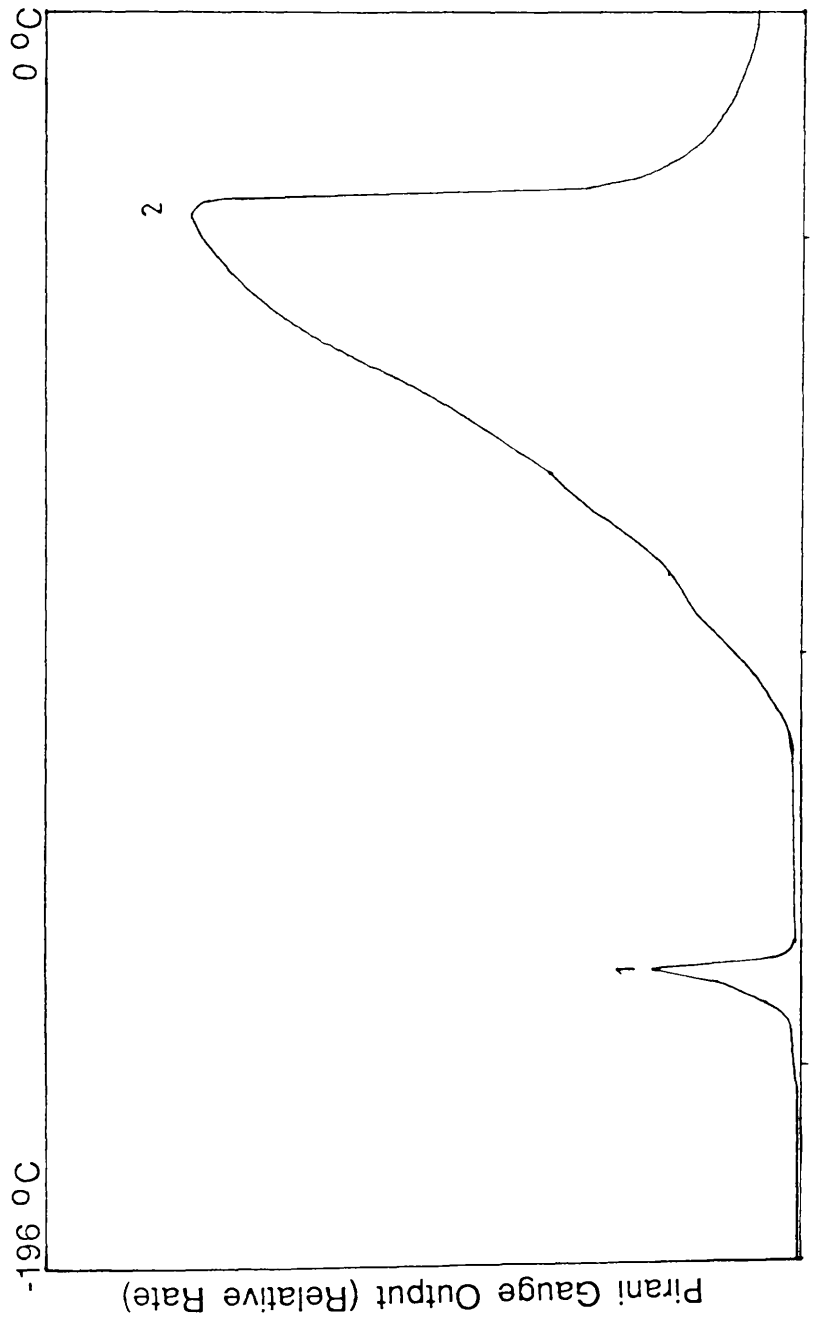


Fig. 6.7. SATVA curve for warm-up from -196 °C to 0 °C of condensable volatile product fraction from degradation to 500 °C under normal TVA conditions of dicarboxyl-terminated Polystyrene. Products were collected in two fractions.

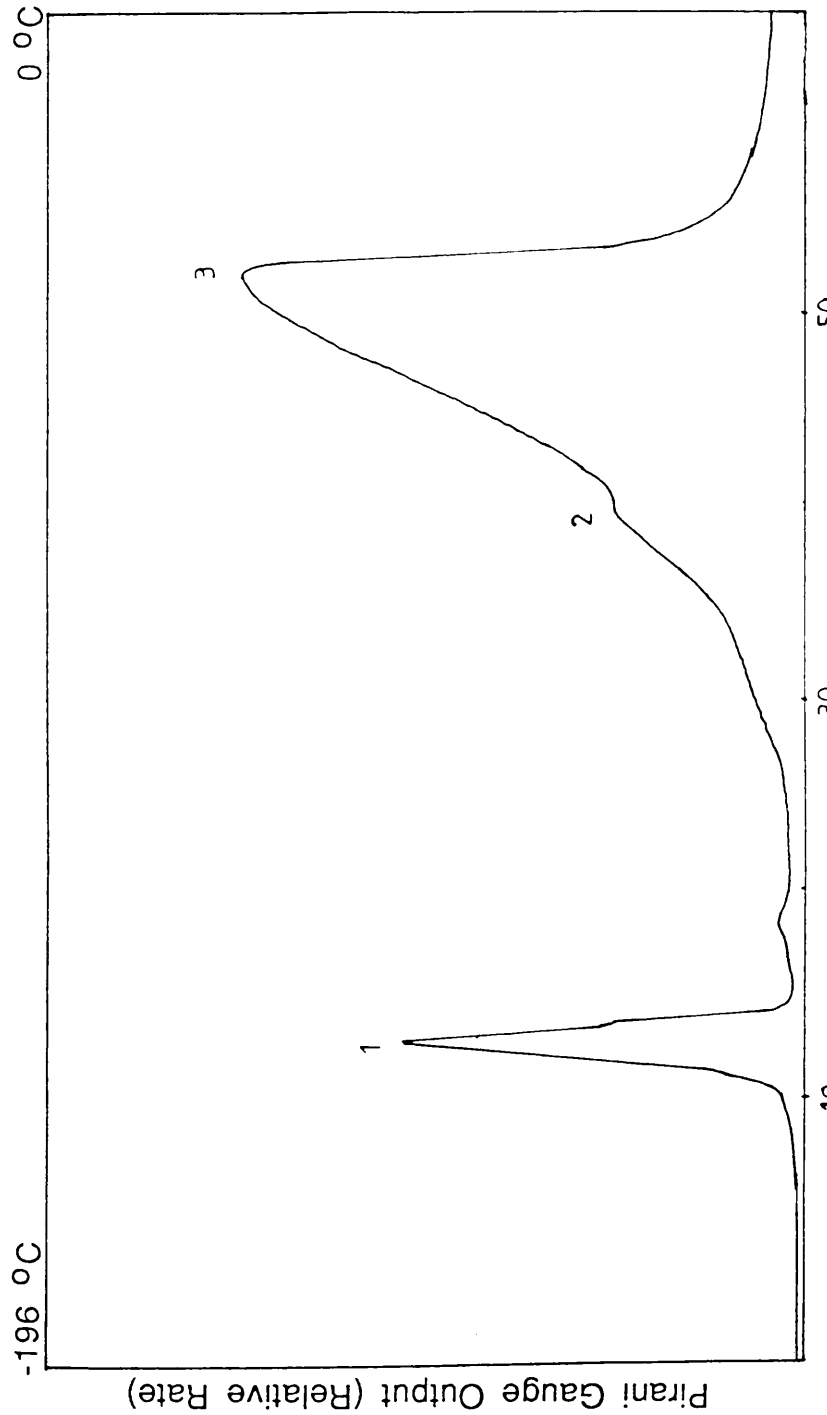


Fig. 6.8. SATVA curve for warm-up from -196 °C to 0 °C of condensable volatile product fraction from degradation to 500 °C under normal TVA conditions of diacid chlorid-terminated Polystyrene. Products were collected in three fractions as indicated.

terminated polystyrene is shown in Fig. 6.9.

The CRF quantities measured gravimetrically were 32.25%, 37.5% and 35.0% in hydroxyl, carboxyl and acid chloride-terminated polystyrene samples, respectively. The weight percentage of CRF was higher in these three polymers than for normal polystyrene. The main CRF materials are short chain fragments (oligomer), which are sufficiently volatile to escape from the hot zone as CRF. Such materials were also observed in normal polystyrene and their mechanism of formation has been explained in Chapter Five. The analysed products from the cold ring fraction of functionally-terminated polystyrenes are summarised in Table 6.4.

2.3.2.3. Condensables as Liquid Fraction

In hydroxyl-terminated polystyrene, all of the degradation products were collected as liquid fraction. The IR spectrum of the liquid fraction was similar to the styrene spectrum, as previously shown on page 80.

In the case of carboxyl-terminated polystyrene, however, the liquid fraction spectrum (Fig.6.9b) also shows a carbonyl absorption band at 1700 cm^{-1} Liquid fractions from all these polymer samples were also analysed by using MS technique. MS chromatograms of carboxyl-terminated polystyrene is shown in Fig. 6.10(a,b).

Further identification of these fractions was carried out by using GC-MS and the chromatograms are illustrated in Fig. 6.11, 6.12 and 6.13, respectively.

It is concluded that toluene, α-methylstyrene, ethylbenzene and benzene are the volatile products next in order of importance to styrene. All the degradation products evolved from these polymer samples degraded to 500 ^{o}C in the TVA system under vacuum using programmed heating are listed in Tables 6.4, 6.6 and

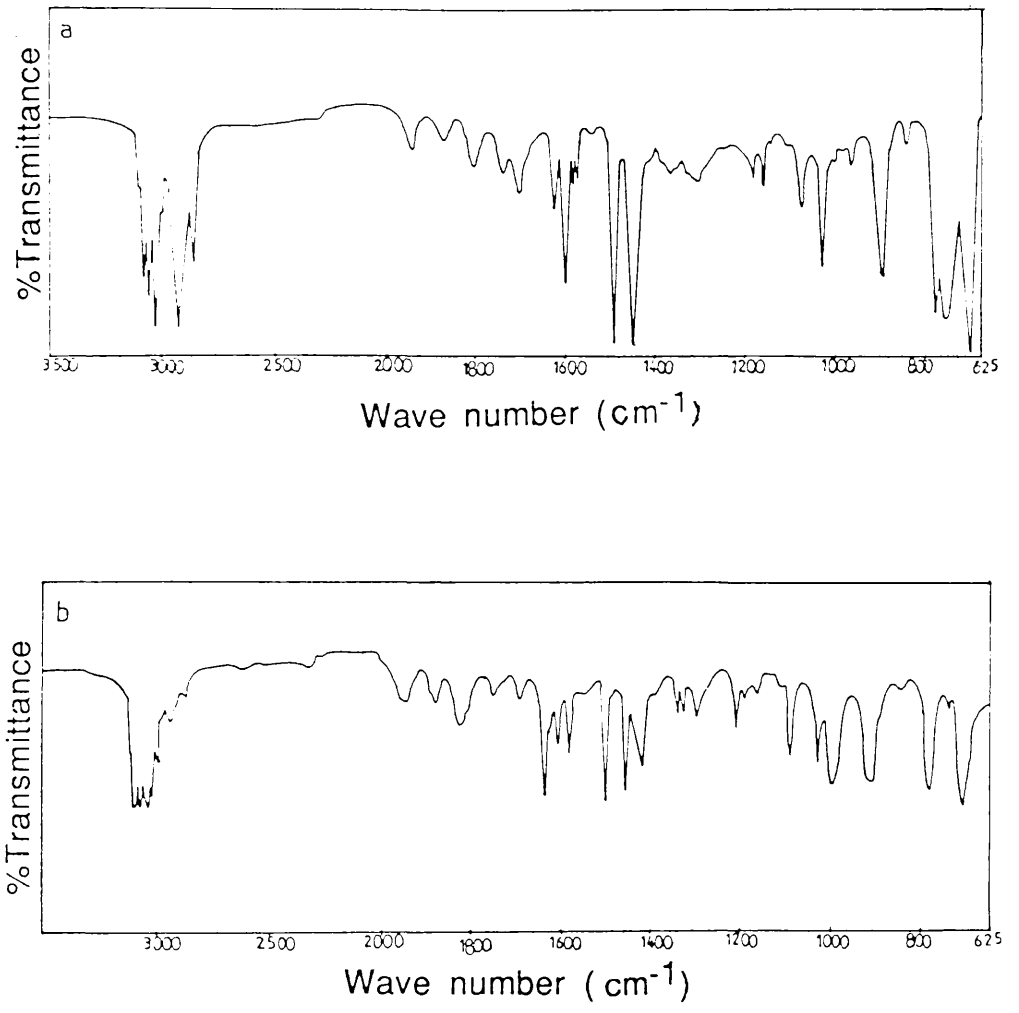


Fig. 6.9. Infrared spectra of cold ring fraction and liquid fraction from degradation of dicarboxyl-terminated Polystyrene to 500 ^{o}C in the TVA system. (a) Cold Ring Fraction (b) Liquid Fraction.

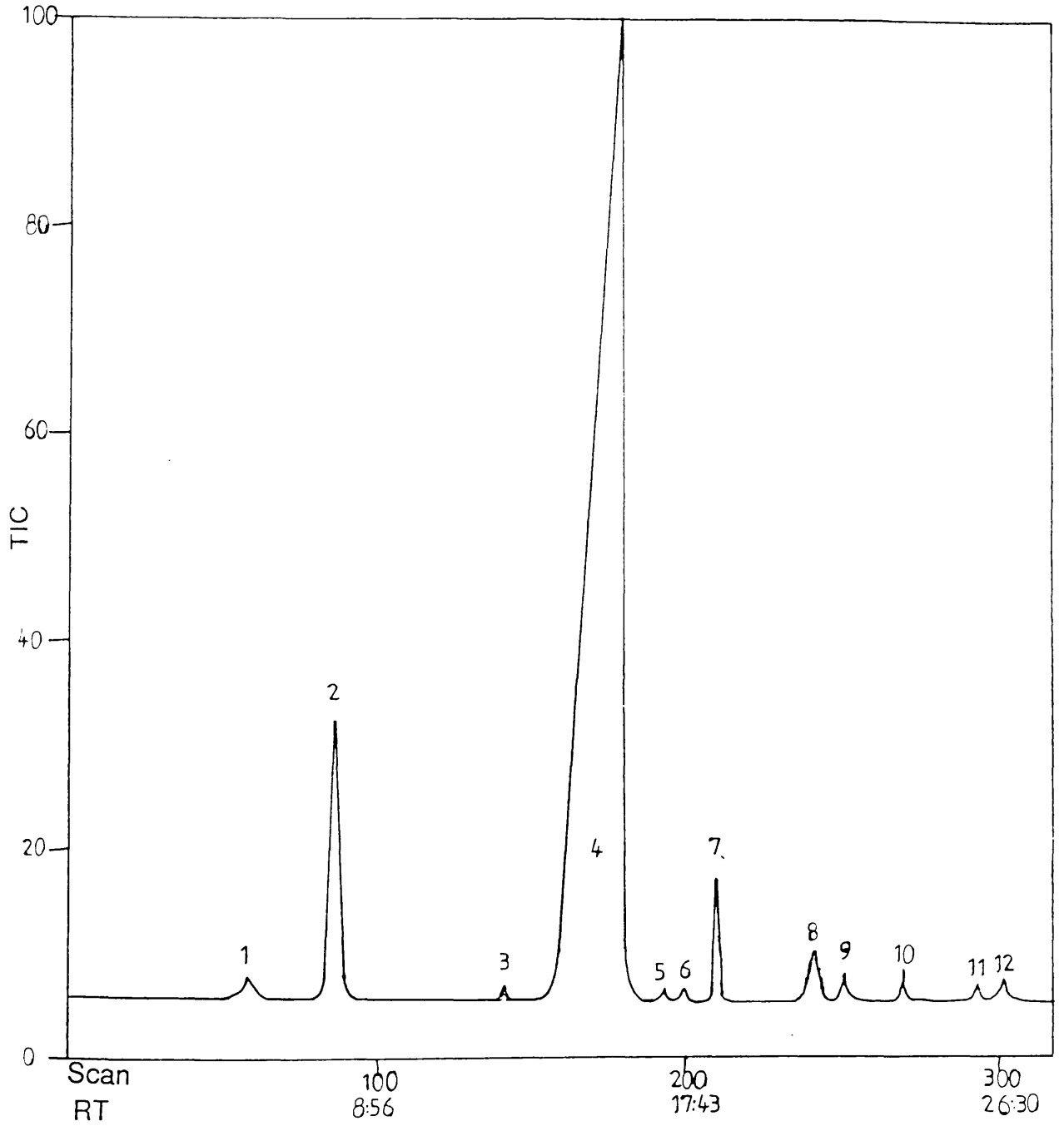


Fig. 6.10. GC data for the volatile liquid fraction from degradation of HO-PS-OH under TVA conditions to 500 ^{o}C.

Assignments: 1; Benzene, 2; Toluene, 3; Ethylbenzene, 4; Styrene, 5; Allylbenzene, 6; Cyclopropylbenzene, 7; α-methylstyrene, 8; Benzaldehyde, 9; Unknown, 10; Benzylalcohol, 11;α-methylbenzylalcohol, 12; Naphthalene.

6.7, respectively.

2.3.2.4. Condensables as Gases

The condensable gaseous products from degradation of the polymer samples to 500 ^{o}C were examined by IR spectroscopy and mass spectrometry after SATVA separation and found to consist of carbon dioxide and HCl gas in the case of diacid chloride-terminated polystyrene. An absorption band at 2070 cm^{-1} due to presence of carbonyl sulphide was also present (Fig. 6.14a). The product giving the second peak of the SATVA trace identified as benzene.

2.3.2.5. Non-Condensable Gases

Carbon monoxide was established as non-condensable product by using Toepler apparatus and analysis by IR and MS.

2.4. Partial Degradation Under TVA Conditions

The acid chloride-terminated polystyrene (80 mg) was degraded to 280 ^{o}C using programmed heating at 10 ^{o}C/min.

Condensable volatile degradative products, collected in a liquid nitrogen trap and separated by SATVA technique, were found to be hydrogen chloride and a trace of carbon dioxide. The involatile residue was a light brown solid with a similar IR spectrum to normal polystyrene but with a very small additional peak at 1695 cm^{-1}.

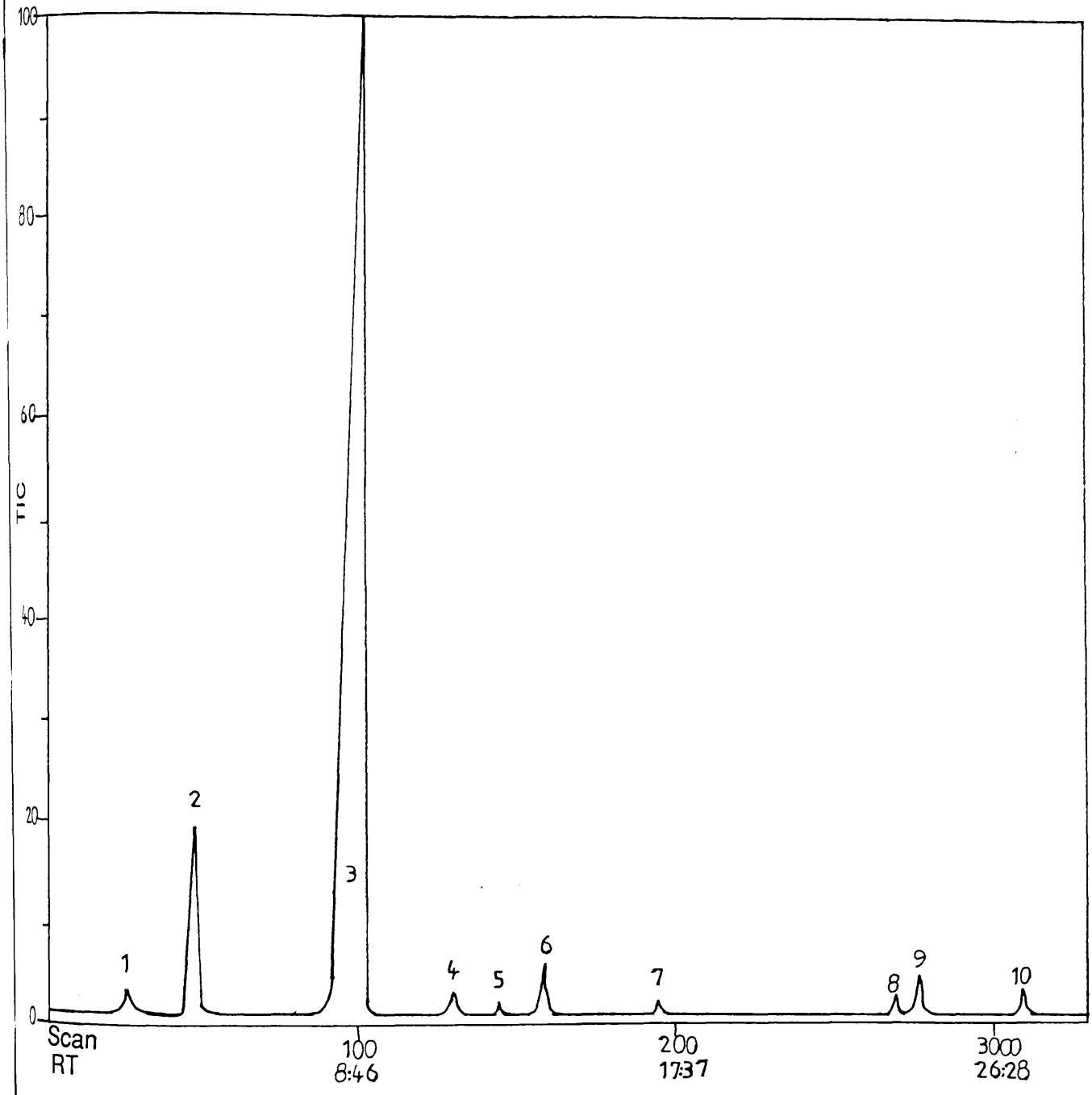


Fig. 6.11. GC data for the volatile liquid fraction from degradation of HO_2C-PS-CO_2H under TVA conditions to 500 ^oC.

Assignments: 1; Benzene, 2; Toluene, 3; Styrene, 4; Allylbenzene,5; unknown, 6; α-methylstyrene 7; Unknown, 8; Phenylacetic acid, 9; Naphthalene, 10; Phenylpropanoic acid.

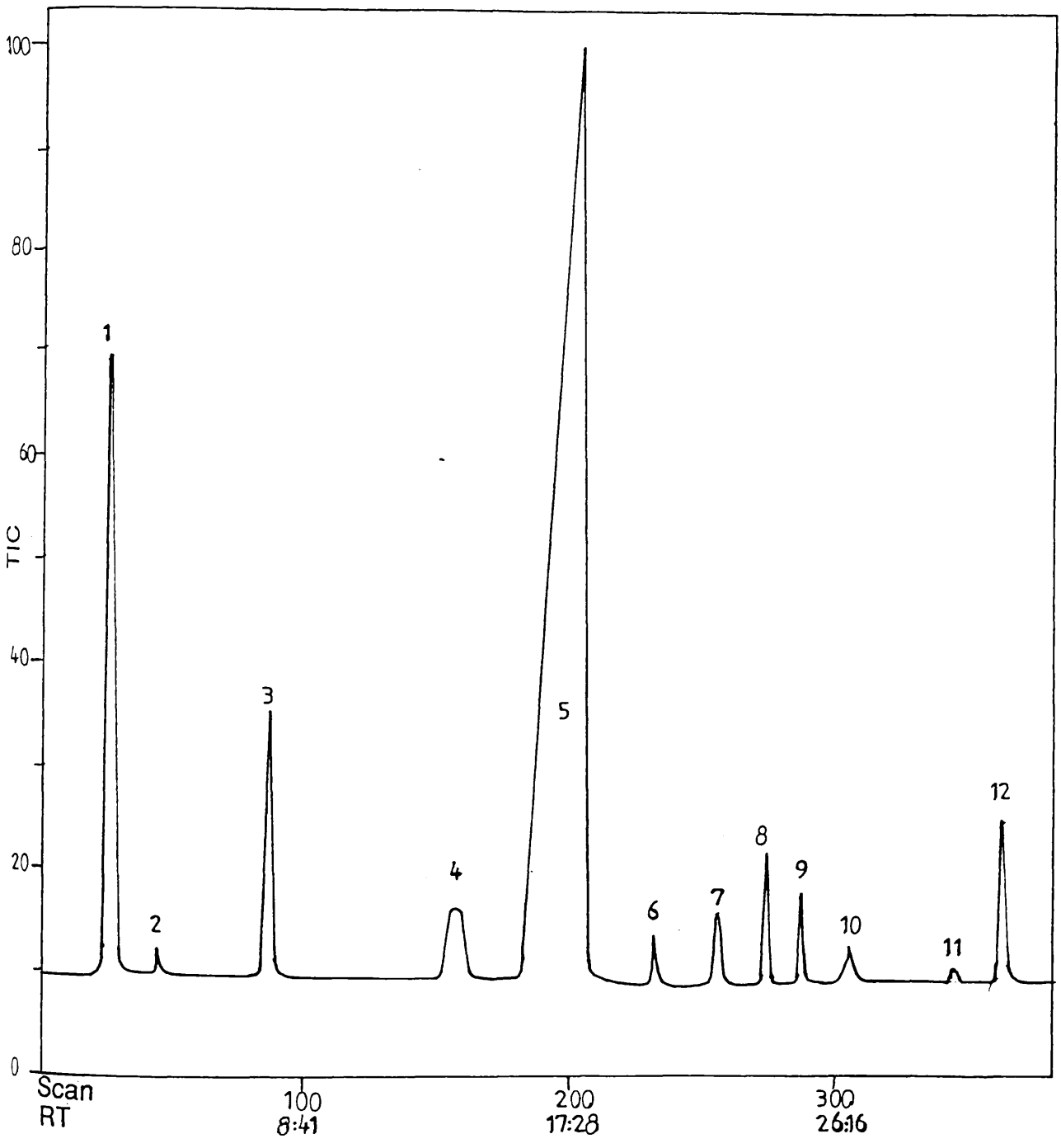
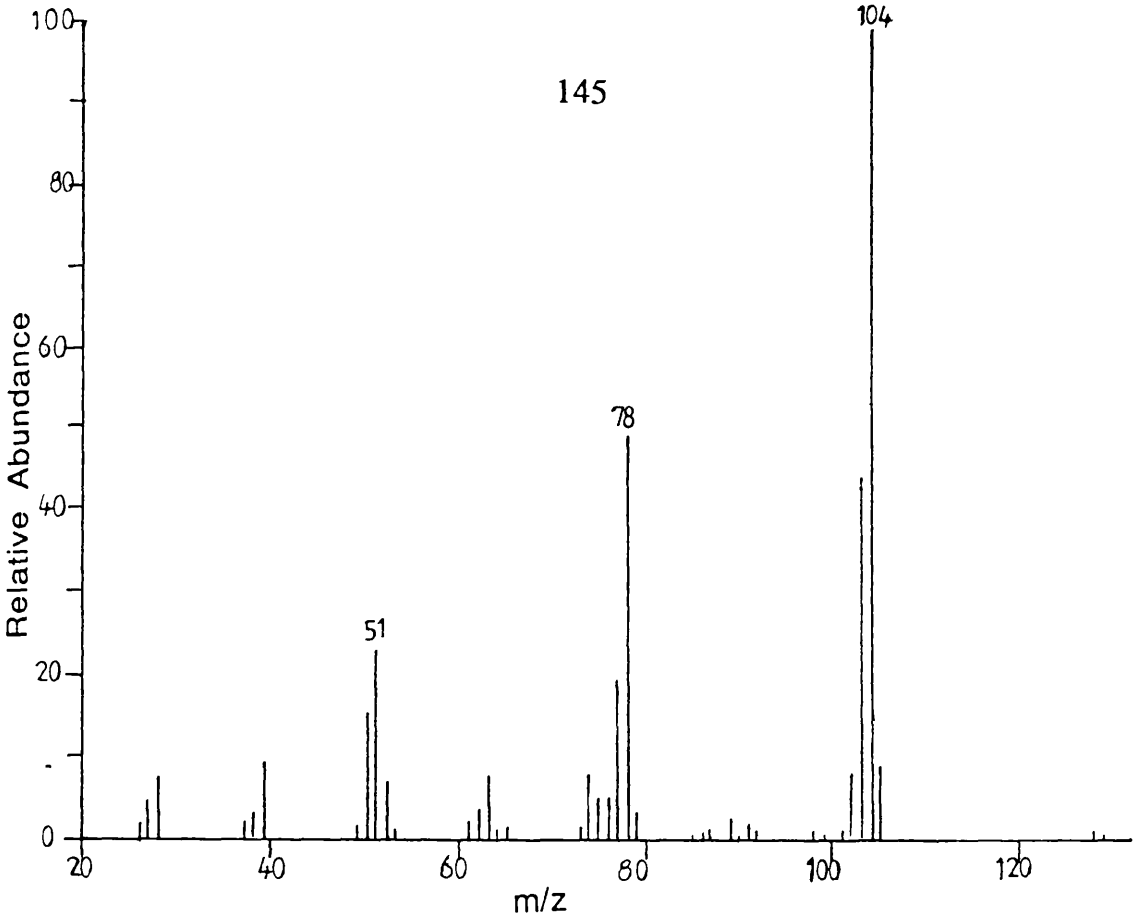


Fig. 6.12. GC data for the volatile liquid fraction from degradation of ClOC-PS-COCl in TVA system under vacuum to 500 ^{o}C.

Assignments: 1; Solvent, 2; Benzene, 3; Toluene; 4; Ethylbenzene; 5; Styrene; 6; Allylbenzene; 7; Isopropylbenzene, 8; α-methylstyrene, 9; 1,2-dichlorobenzene, 10; ß-chlorostyrene, 11; Benzaldehyde, 12; Naphthalene.



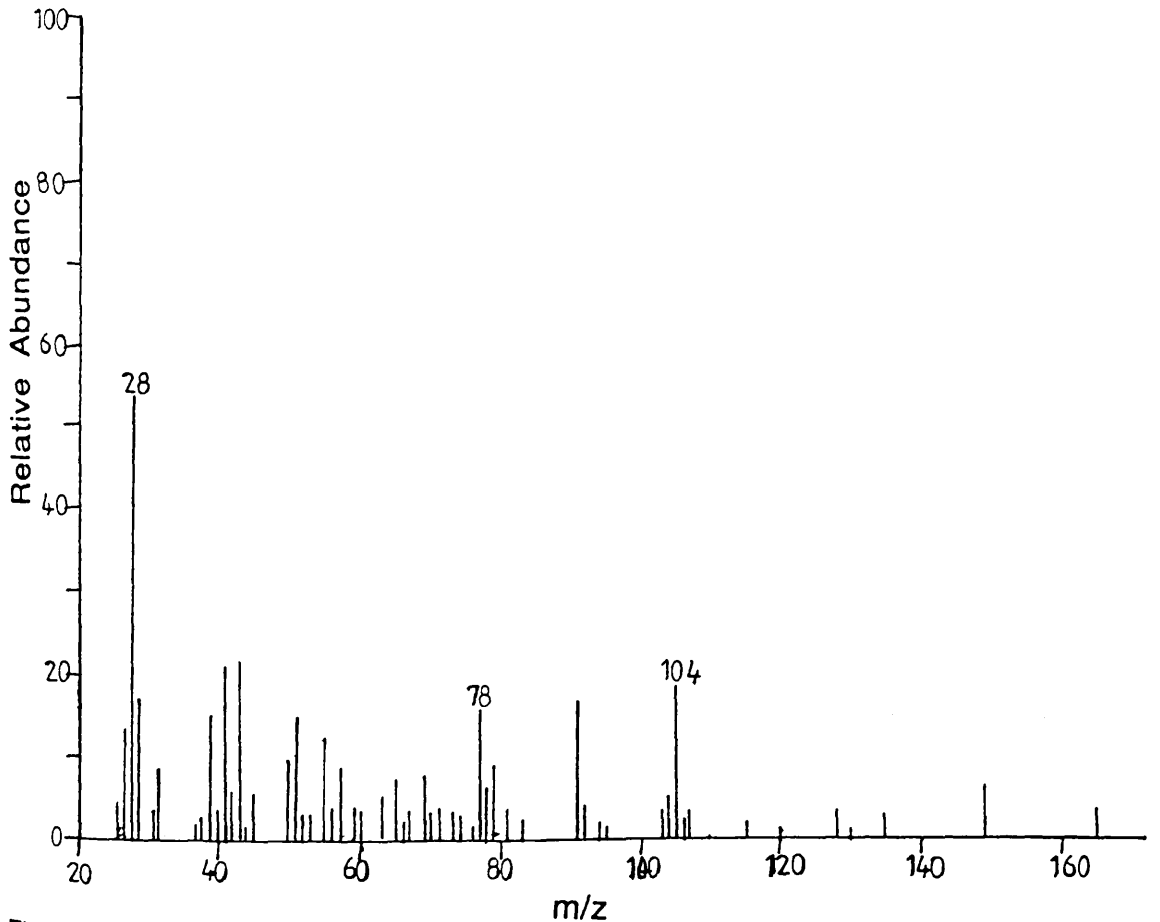
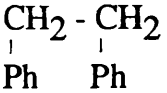
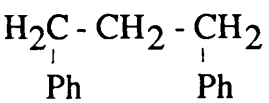
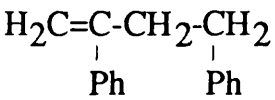
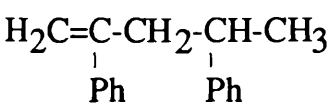
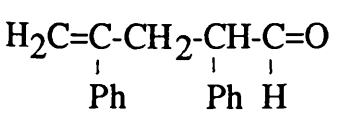
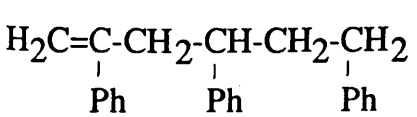
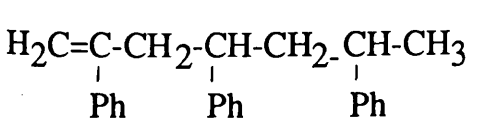


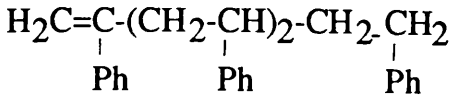
Fig. 6.13. Mass spectra of liquid fraction from degradation to 500 °C under normal TVA conditions of dicarboxyl-terminated Polystyrene.

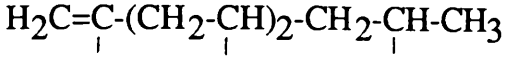
(a) Probe Temperature 170 °C.

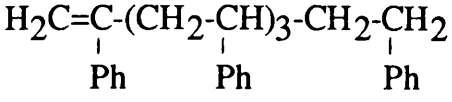
(b) Probe Temperature 240 °C.

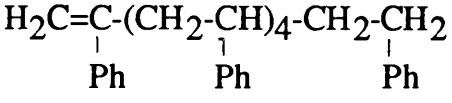
Table 6.4 Products Identified in the Cold Ring Fractions from Degradation of Hydroxyl, Carboxyl and Acid chloride-Terminated Polystyrene Samples Under Normal TVA Conditions to 500 ^{o}C.

Product	Name	m/e
	1,2-diphenyl ethane	182
	1,3-diphenyl propane	196
	styrene dimer	208
	dimer with extra methyl group	222
	dimer with carbonyl group	236
	styrene trimer	312
	trimer with extra methyl group	326

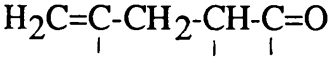

tetramer 416


tetramer with extra methyl group 434

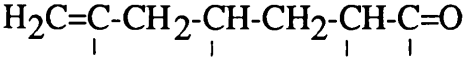

pentamer 520


hexamer 624

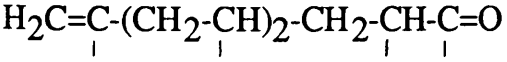
*


dimer with carboxyl group 253

*


trimer with carboxyl group 357

*


tetramer with carboxyl group 461

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Products only identified from carboxyl-terminated polystyrene sample.

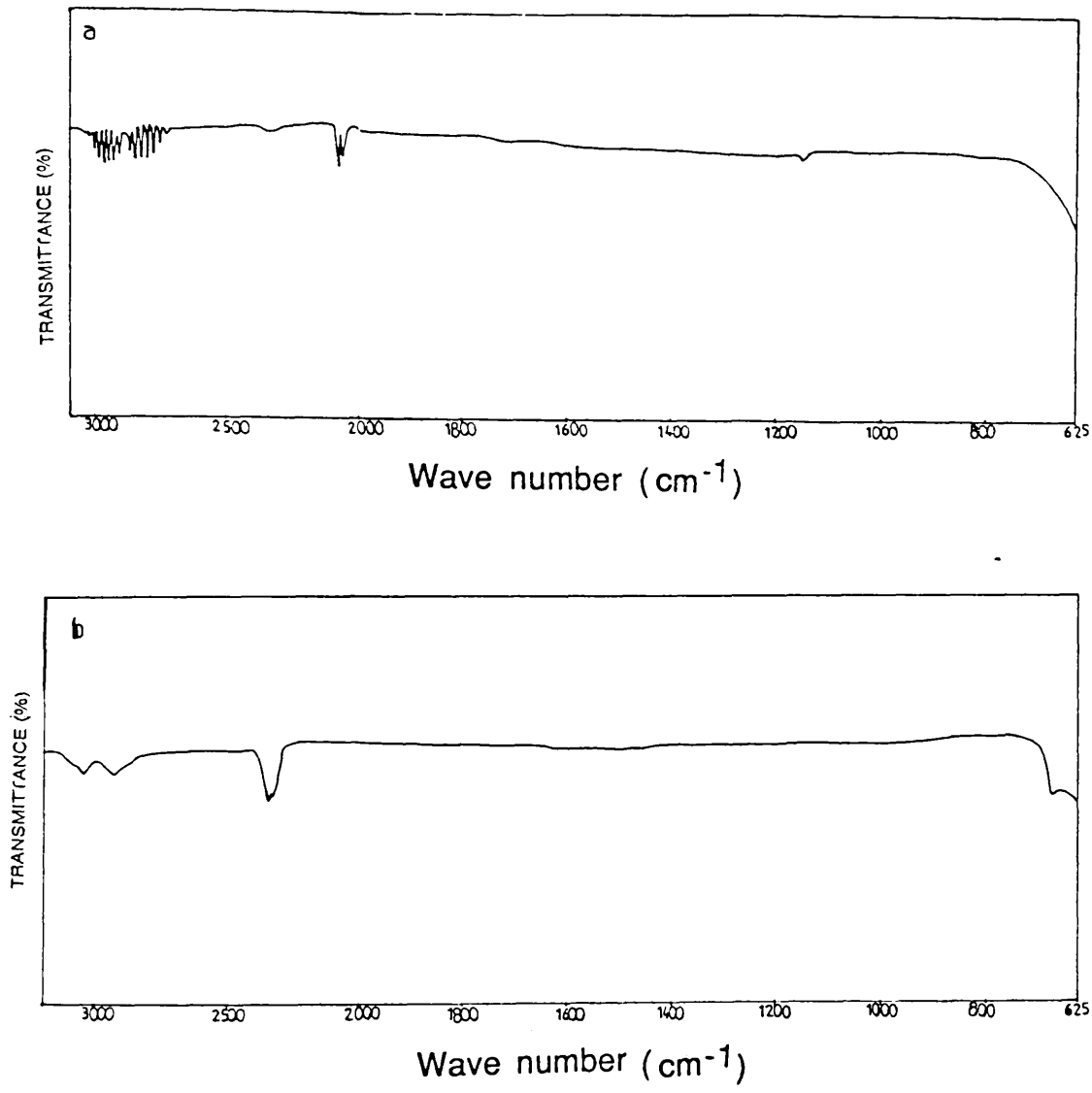


Fig. 6.14. Infrared spectra of gaseous volatile products from degradation to 500 ^{o}C under TVA conditions.

(a) HCl and S=C=O (Degradation products of ClOC-PS-COCl)

(b) CO_2 (Degradation Product of HO_2C-PS-CO_2H)

Table 6.5 Products of Degradation of HO-PS-OH to 500 °C at 10 °C/min Under TVA Conditions.

Condensable Volatile Products at -196 °C		Cold Ring Fraction		
Gases		Liquid Fraction		
IR	IR,MS	GC	GC-MS	IR,MS
CO_2 (trace amount)	Styrene α-methyl styrene Toluene Benzene Propyl benzene Naphth-alene Benzyl alcohol	Styrene Toluene α-methyl styrene Benzyl alcohol α-methyl benzyl alcohol Ethyl benzene Propyl benzene	Styrene α-methyl styrene Benzene Toluene Allyl benzene Propyl benzene Ethyl benzene Benzyl alcohol α-methyl benzyl alcohol Naphth-alene Cyclopropyl benzene	Mainly short chain fragm-ents but few short chain frag-ments containing carbonyl groups

Table 6.6 Products of Degradation of HO_2C-PS-CO_2H to 500 °C Under TVA Conditions Using Programmed Heating at 10 °C/min.

Non-condensable products at -196 °C	Condenabsle volatile products at -196 °C				Cold Ring Fraction
	Gases	Liquid Fraction			
IR,MS	IR,MS	IR,MS	GC	GC-MS	IR,MS,TLC
CO	CO_2	Styrene α-methyl styrene Toluene Phenyl propano-ic acid Phenyl butanoic acid Ethyl benzene Propyl benzene Phenyl acetic acid Naphth-alene	Styrene Benzene Toluene α-methyl styrene Phenyl propano-ic acid Phenyl acetic acid Ethyl benzene Naphth-alene	Styrene Toluene α-methyl styrene Allyl benzene Ethyl benzene Benzene Phenyl acetic acid Phenyl propan-oic acid Naphth-alene	Short chain fragments containing carbonyl and carboxyl groups

Table 6.7 Products of Degradation of ClOC-PS-COCl to 500 °C Under TVA Conditions Using Programmed Heating at 10 °C/min.

Non-condensable products at -196 °C	Condensable volatile products at -196 °C				Cold Ring Fraction
	Gases	Liquid Fraction			
IR,MS	IR,MS	IR,MS	GC	GC-MS	IR,MS,TLC
CO	CO_2 HCl O=C=S	Styrene Toluene Ethyl benzene α-methyl styrene Benzene Chloro benzene Benzald-ehyde Dichloro benzene Naphth-alene	Styrene α-methyl styrene Toluene Benzene Chloro-benzene Ethyl benzene Allyl benzene Naphth-alene	Styrene Benzene α-methyl styrene Toluene Allyl benzene 1,2-di-chloro benzene ß-Chloro styrene Ethyl benzene Naphth-alene Benzald-ehyde Isopropyl benzene	Short chain fragments containing carbonyl groups

3. ISOTHERMAL HEATING EXPERIMENTS

3.1. Isothermal Heating at 300°, 350°, and 420 °C

In this investigation 150 mg samples of the hydroxyl, carboxyl and acid chloride-terminated polystyrene samples were each degraded isothermally under vacuum in TVA system at 300°, 350° and 420 °C successively for 15 min. The condensable volatile liquid products were collected in a cold finger at each temperature and examined by using the GC-MS technique. The chromatograms for the GC-MS investigations at 350 °C of these fractions from degradation of hydroxyl, carboxyl and acid chloride-terminated polystyrene samples are given in Figs. 6.15, 6.16 and 6.17, respectively. All the products identified in the degradation of these three polymers, isothermally heated at 300°, 350°, and 420°C are summarised in Table 6.8.

3.2. Structural Changes and Molecular Weight at 300 °C

The functionally-terminated polystyrene polymers were each heated isothermally at 300 °C under TVA conditions (250 mg samples) for different periods of time to investigate the structural changes and to determine any change in the average molecular weights ($\bar{M}n$).

Structural changes were observed by using FT-IR spectroscopy. Samples were heated at 300 °C for 15, 30, 60 and 90 mins successively and spectra were recorded at each stage.

In carboxyl-terminated polystyrene the carboxyl group absorption decreased with time of heating. There was no band at 1790 cm^{-1} in the spectrum of acid chloride-terminated polystyrene after heating at 300 °C for 15 min but an additional small band at 1695 cm^{-1} was observed. The rest of the spectra were

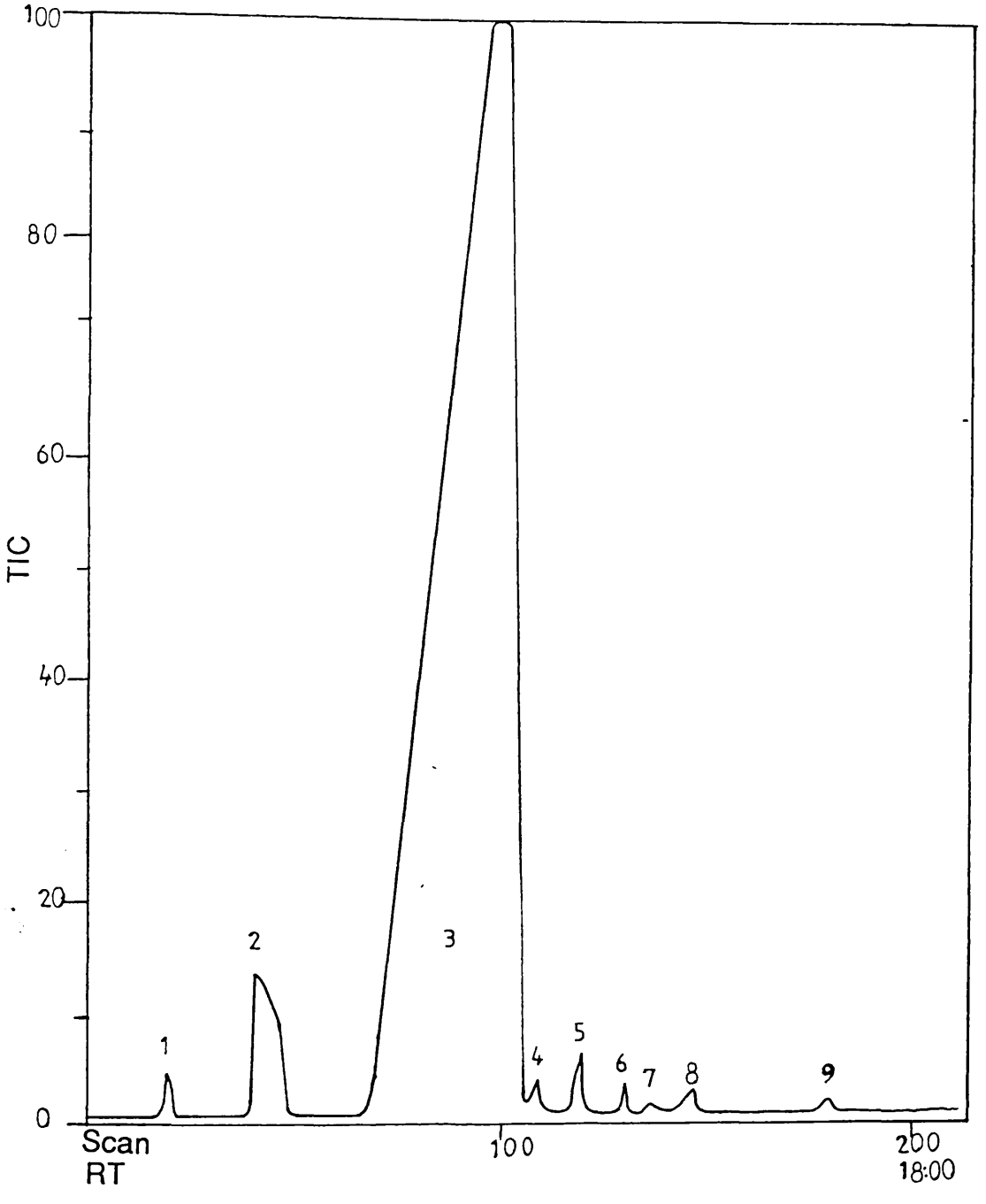


Fig. 6.15. GC data for the volatile liquid fraction for degradation of HO-PS-OH in the TVA system under vacuum for 15min at 350 ^{o}C.

Assignments: 1; Benzene, 2; Toluene, 3; Styrene, 4; Allylbenzene, 5; ∝-methylstyrene, 6; Cyclopropylbenzene, 7; 4-phenyl-1-butene, 8; Benzaldehyde, 9; Dimethylindene.

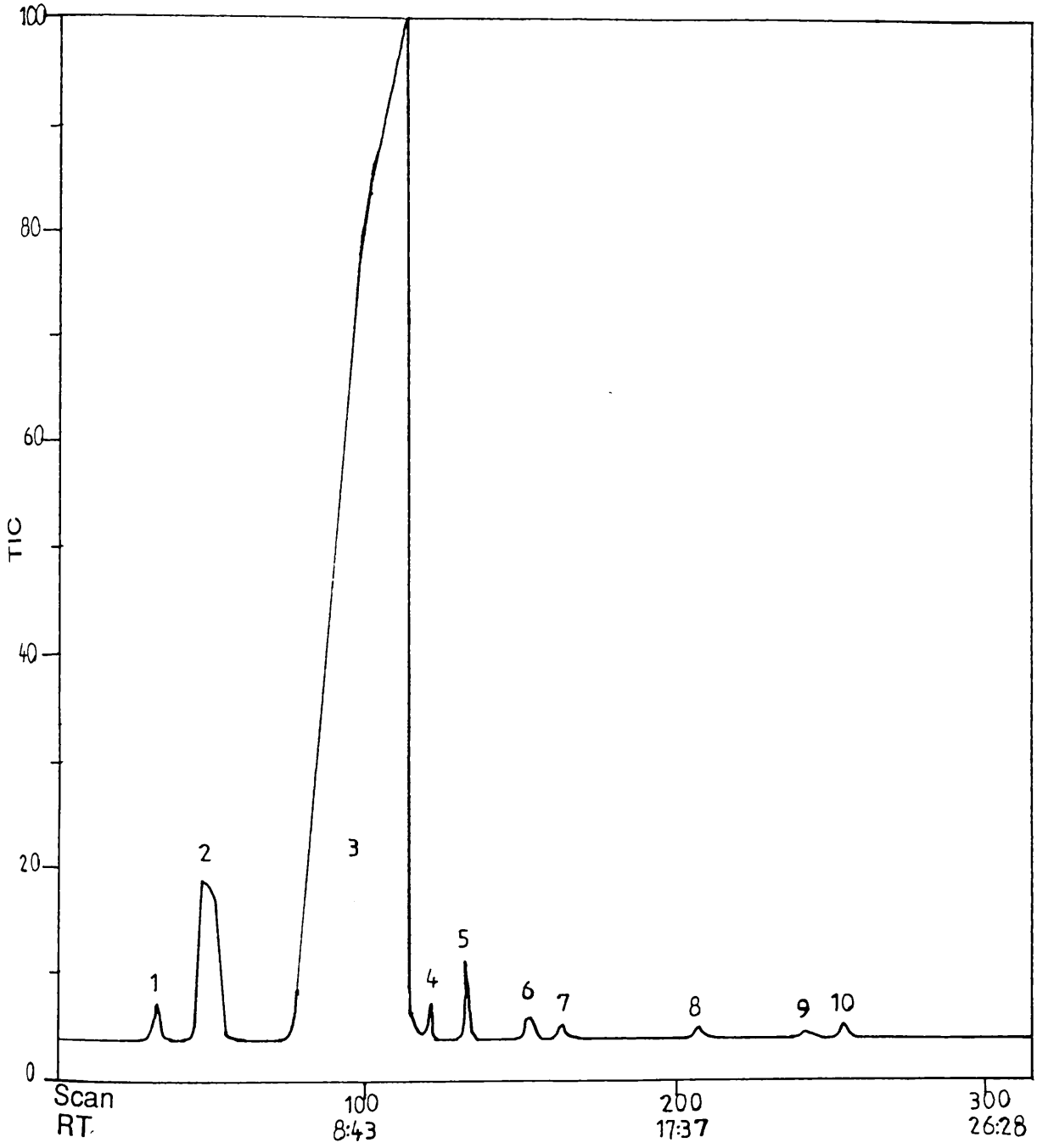


Fig. 6.16. GC data for the volatile liquid fraction from degradation of HO_2C-PS-CO_2H in the TVA system under vacuum for 15 min at 300 ^oC.

Assignments: 1; Benzene, 2; Toluene, 3; Styrene, 4; Allylbenzene, 5; ∝-methylstyrene, 6; Indane, 7; 4-phenyl-1-butene, 8; 2,3-dimethylindene, 9; Unknown, 10; Phenylpropanoic acid.

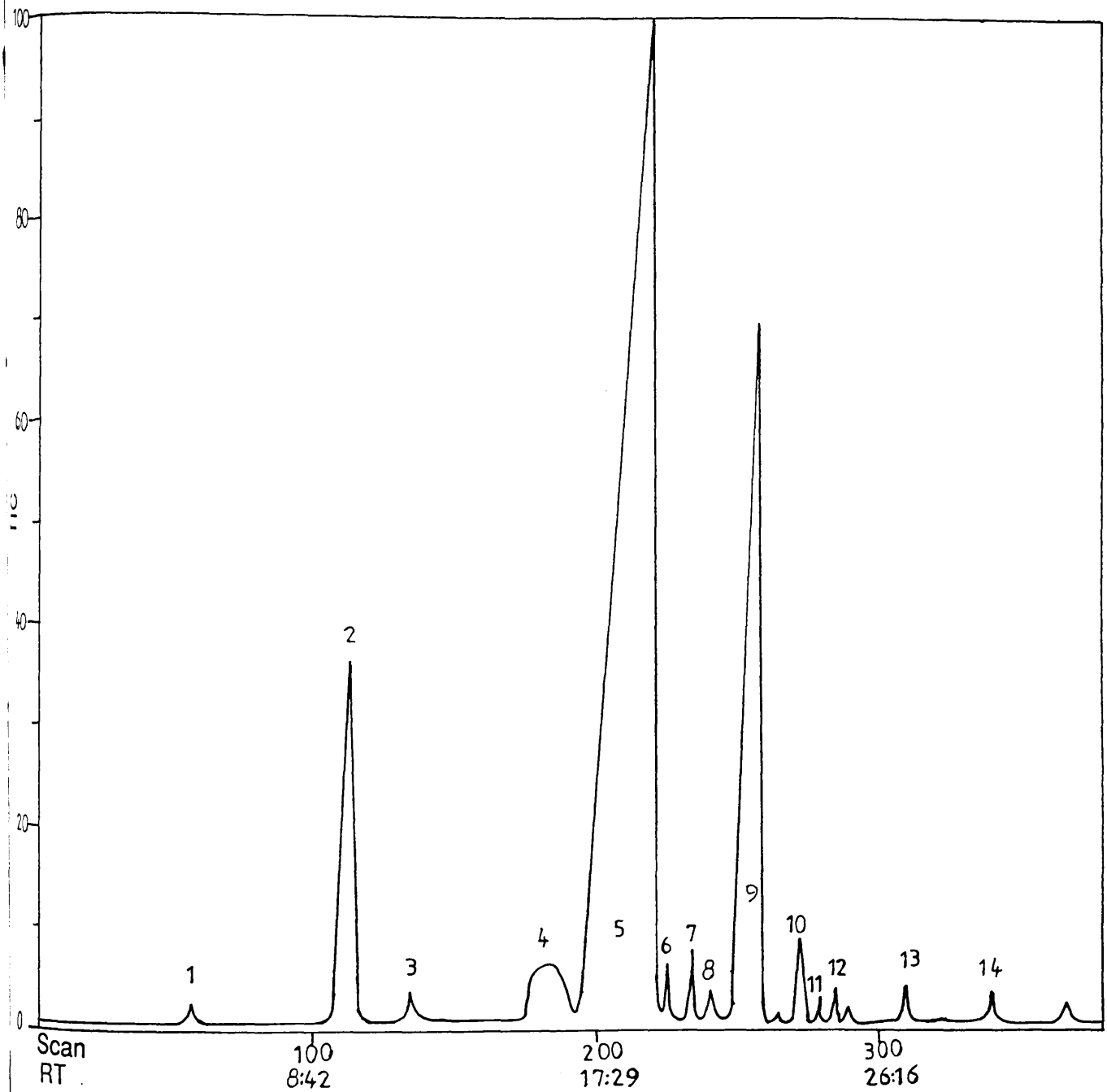


Fig. 6.17. GC data for the volatile liquid fraction from degradation of ClOC-PS-COCl in the TVA system under vacuum for 15 min at 350 ^{o}C.

Assignments:1; Benzene, 2; Toluene, 3; Chlorobenzene, 4; Ethylbenzene, 5; Styrene, 6; Unknown, 7; Allylbenzene, 8; Propylbenzene, 9; α-methylstyrene, 10; Indane, 11; 4-phenyl-1-butene, 12; Methylindane, 13; Methylindene, 14; Naphthalene.

Table 6.8 GC-MS Results for Condensable Volatile Liquid Products Evolved from Hydroxyl, Carboxyl and Acid chloride-Terminated Polystyrene Heated Isothermally at 300°, 350° and 420 °C for 15 min in Each Case Under Normal TVA Conditions.

	HO-PS-OH	HO_2C-PS-CO_2H	ClOC-PS-COCl
Common products evolved for all polymers at all temperatures	Styrene, Toluene, α-methylstyrene,		
300 °C	Benzyl alcohol α-methyl- benzyl alcohol Allylbenzene Naphthalene Isopropyl benzene Cyclopropyl benzene	Allylbenzene Ethylbenzene Benzene Phenyl- acetic acid Phenylpropa- noic acid	Propylbenzene Ethylbenzene Allylbenzene Benzaldehyde Indane Methylindane
350 °C	4-phenyl- 1-butene Benzaldehyde Dimethylindane Methylindene	Indane 4-phenyl- 1-butene 2,3-dimethyl indene Benzene	Allylbenzene Propylbenzene Chlorobenzene 4-phenyl-1-butene Benzene
420 °C	Allyl- benzene Indene	Ethylbenzene 2-methyl indene	Ethylbenzene ß-chlorostyrene

similar to those of the original polymers in nearly every respect.

The number-average molecular weight ($\bar{M}n$) and heterogeneity index ($\bar{M}w/\bar{M}n$) for the three polymer samples after various periods of heating at 300 °C under TVA conditions are listed in Table 6.9.

3.3. Gravimetric Analysis Under TVA Conditions and Under Nitrogen Atmosphere

The thermal stability of polystyrene samples with different groups was further studied by heating the sample isothermally under TVA conditions at 300 °C and in the thermobalance under dynamic nitrogen at 290 °C.

The percentage weight loss vs time for hydroxyl, carboxyl, and acid chloride-terminated and normal polystyrene samples is plotted in Fig. 6.18.

Gravimetric measurements at 300 °C under TVA conditions are illustrated in Fig. 6.19. Both TG (Fig. 6.18) and TVA (Fig. 6.19) show that hydroxyl-terminated polystyrene is slightly less stable than normal polystyrene and that carboxyl-terminated polystyrene is considerably less stable. Acid chloride-terminated polymer is initially the least stable of all, but after this early volatilisation (10-15%, 1 hour), decomposition behaviour lies between that of hydroxyl and carboxyl-terminated polystyrene.

Camino et al.[85-87] have examined the thermal behaviour of polystyrene with chloromethoxyphosphate groups (TPPS) at the chain ends. They observed that these chains ends underwent a condensation at relative low temperature (200 °C) with evolution of CH_3Cl. They also found that the thermal behaviour of polystyrene and TPPS is quite similar.

Table 6.9 Molecular weight changes in Functionally-Terminated Polystyrene, degraded isothermally at 300 ^{o}C for Various Times Under TVA Conditions.

Polymer	HO-PS-OH	HO_2C-PS-CO_2H	ClOC-PS-COCl
$\bar{M}n$ after 15 min	6,743	6,124	10,620
$\bar{M}w/\bar{M}n$	1.52	1.84	1.90
$\bar{M}n$ after 30 min	9,210	7,999	10,420
$\bar{M}w/\bar{M}n$	1.74	1.72	1.8
$\bar{M}n$ after 60 min	10,200	8,209	9,335
$\bar{M}w/\bar{M}n$	1.9	1.54	1.6
$\bar{M}n$ after 90 min	3,341	2,334	4,323
$\bar{M}w/\bar{M}n$	1.3	1.8	1.5

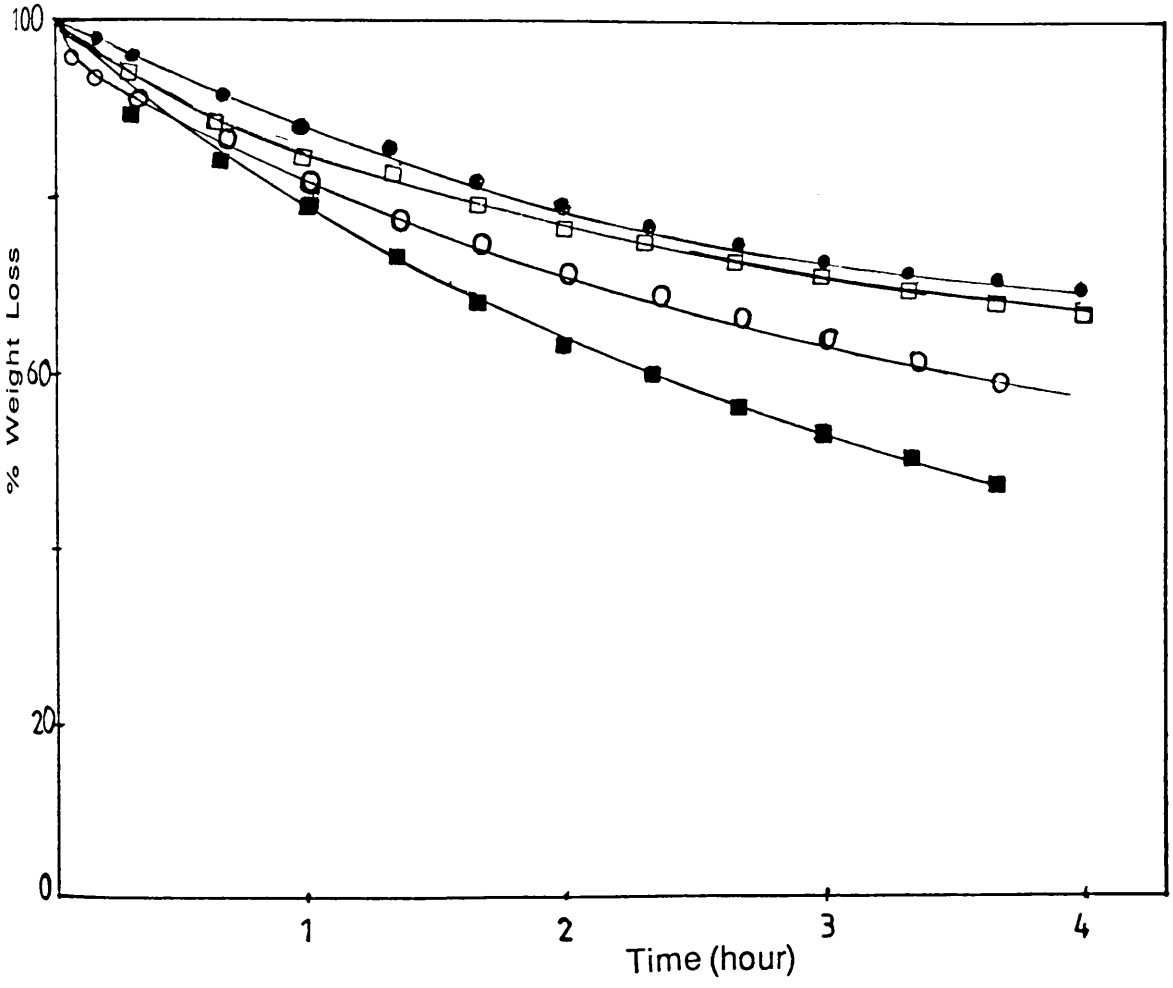


Fig. 6.18. The curves of weight loss vs time for functionally-terminated Polystyrene, degraded isothermally at 290 ^{o}C under dynamic nitrogen atmosphere, in the thermobalance.

Keys: ▫HO-PS-OH, ▪HO_2C-PS-CO_2H, ○ClOC-PS-COCl ●PS

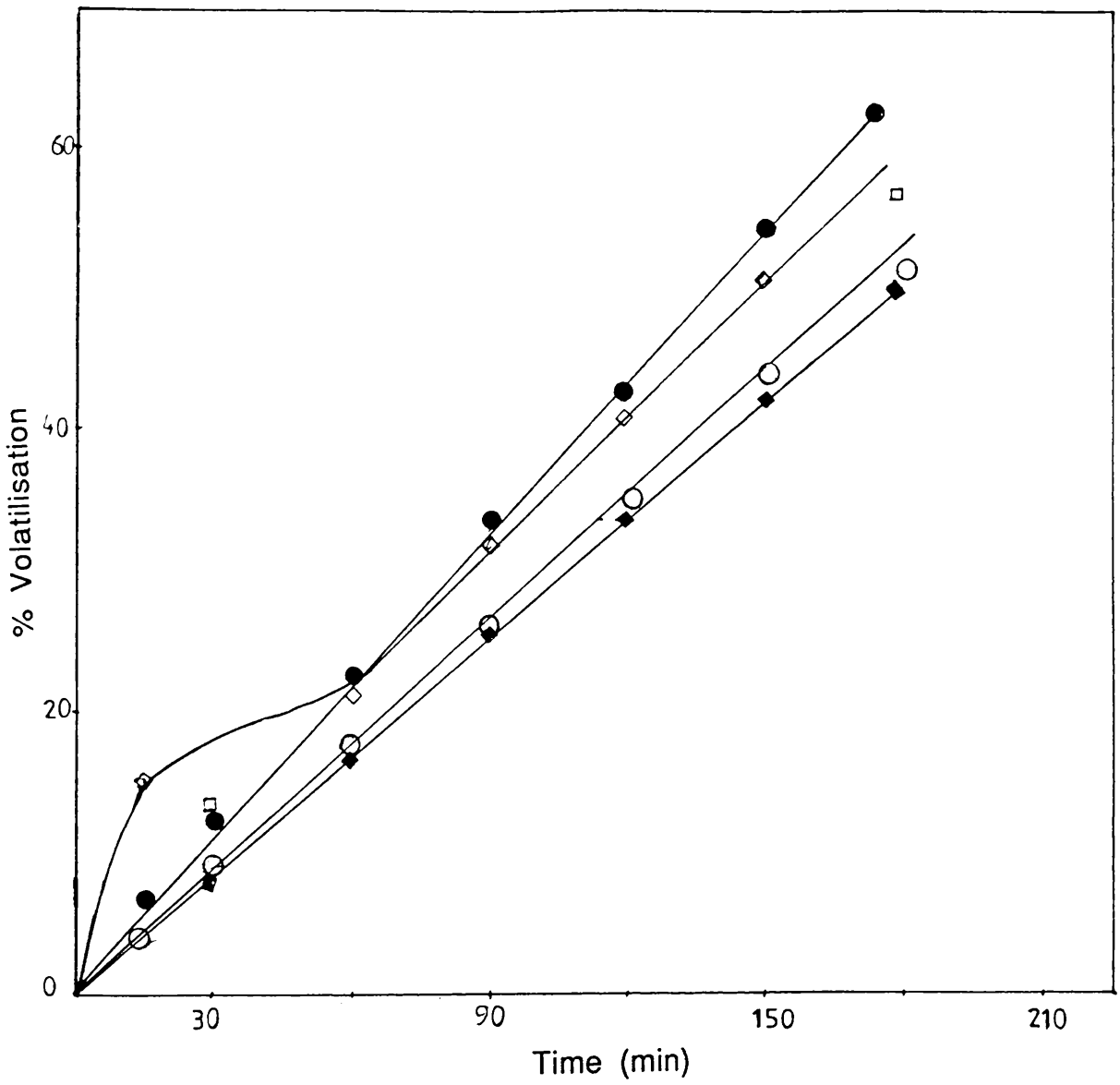


Fig. 6.19. Gravimetric data for volatilisation of functionally-terminated Polystyrene, degraded isothermally at 300 °C under vacuum in the TVA system, as a funation of time.

Keys: ○HO-PS-OH, ●HO_2C-PS-CO_2H, □ClOC-PS-COCl ■PS

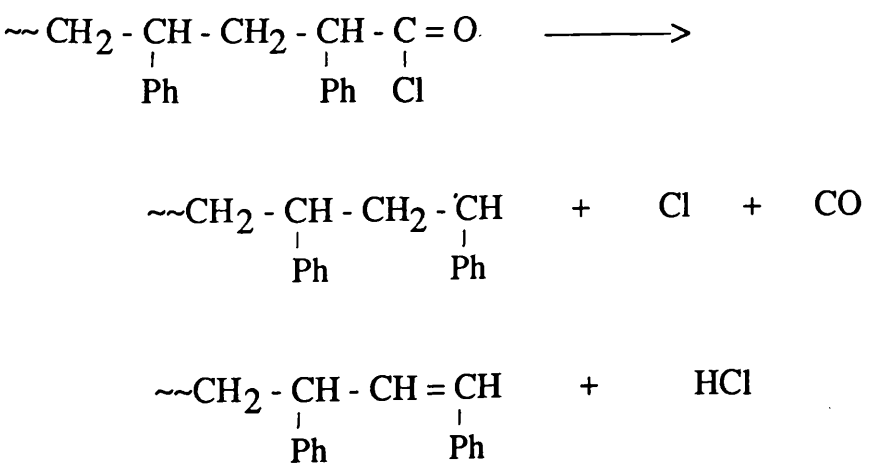
4. MECHANISM OF DEGRADATION

The degradation behaviour of normal polystyrene has already been discussed in Chapter Five.

Degradation of polystyrene begins below 300 ^{o}C by chain scission to generate macroradicals A and B which disproportionate radicals A and B to give benzylic and vinylidene chain ends. Above 300 ^{o}C depolymerisation gives styrene as a major product and dimer and trimer are formed in small amount by intramolecular transfer. Toluene and∝-methylstyrene are minor volatile products. Trace products such as dimethylindene, dimethylindane and 4-phenyl-1-butene are produced from head to head linkages in the polymer. The mechanism has been discussed on page 114.

Below 300 ^{o}C, only chain scission and disproportionation of the macroradicals occur in hydroxyl and carboxyl-terminated polystyrene but in case of acid chloride-terminated polystyrene the additional process of evolution of HCl occurs.

At temperatures below 300 ^{o}C, dehydrochlorination occurs by end group scission and the most obvious pattern of HCl would be:



Chlorobenzene and dichlorbenzene were also identified as minor products in degradation of polymer to 500 ^{o}C under TVA conditions. Further chain scission is expected to occur at temperature higher than 300 ^{o}C, to produce monomer (styrene), and oligomers (dimer, trimer and tetramer).

In hydroxyl and carboxyl-terminated polystyrene samples the condensable and non-condensable volatile products were evolved at above 300 ^{o}C as for normal polystyrene.

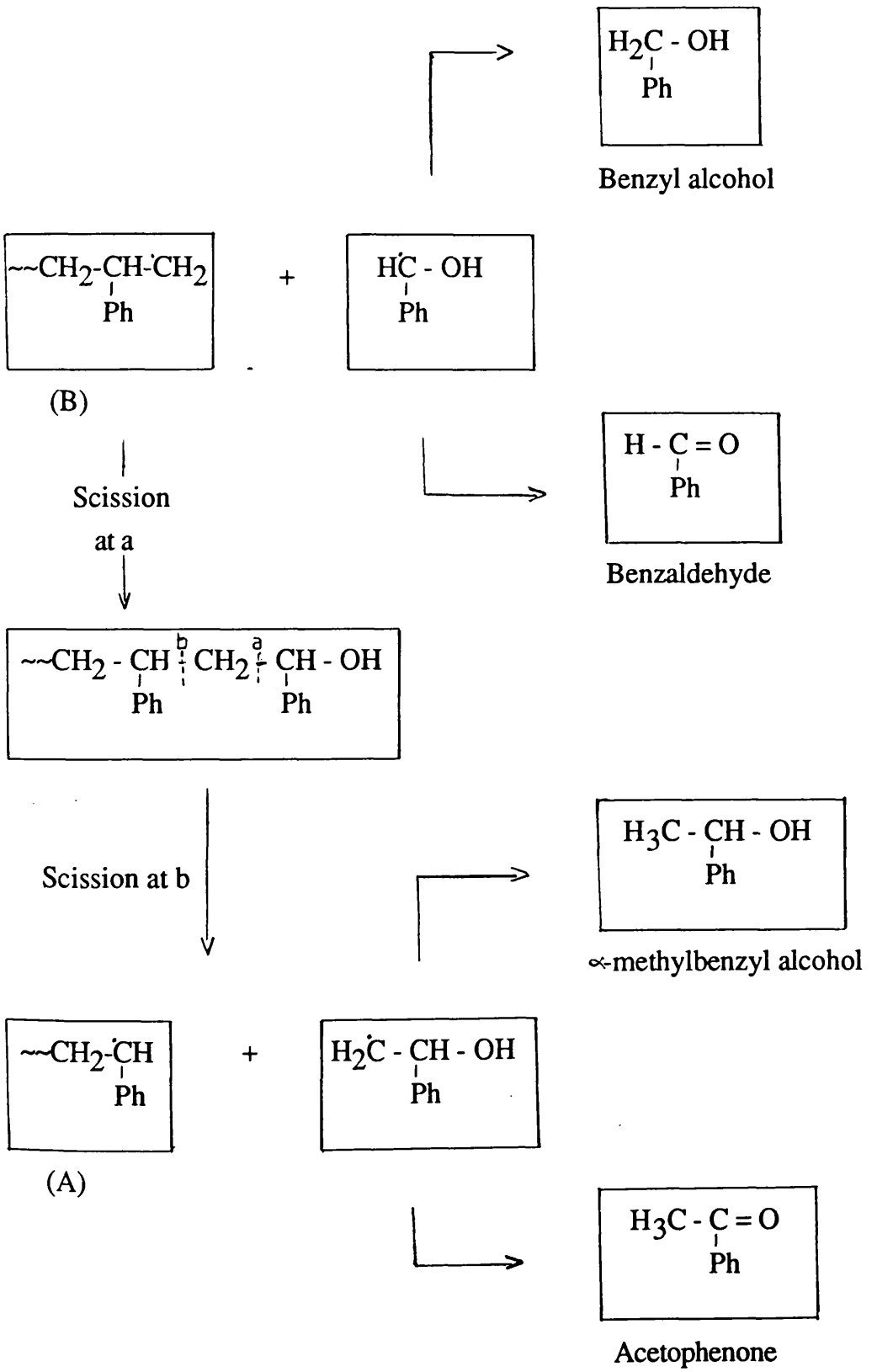
The proposed mechanisms of formation of the minor products of hydroxyl, carboxyl, and acid chloride-terminated polystyrene to 500 ^{o}C under TVA conditions are given in schemes 1, 2 and 3, respectively.

5. CONCLUSIONS

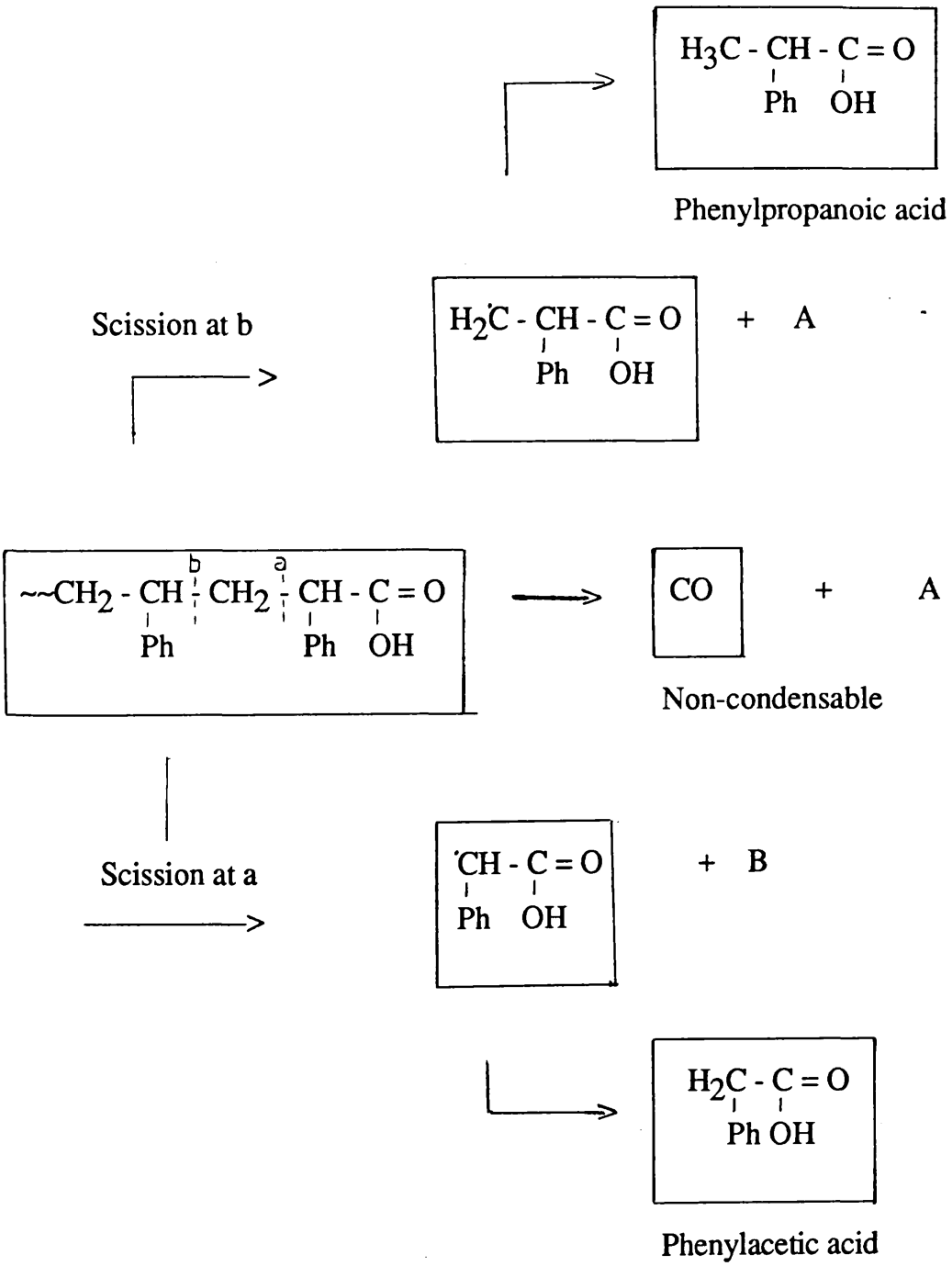
Although the thermal behaviour of the hydroxyl, carboxyl and acid chloride polymers is rather similar, small differences from normal polystyrene are revealed by TVA and TG.

The temperature of the maximum rate of evolution of products from the major degradation processes of these three polymer samples under programmed heating are slightly lower than that of normal polystyrene. The main mechanism similar to normal polystyrene can be proposed for the degradation of these polymers. The acid chloride terminated polystyrene also provides some additional points of weakness at which degradation begins.

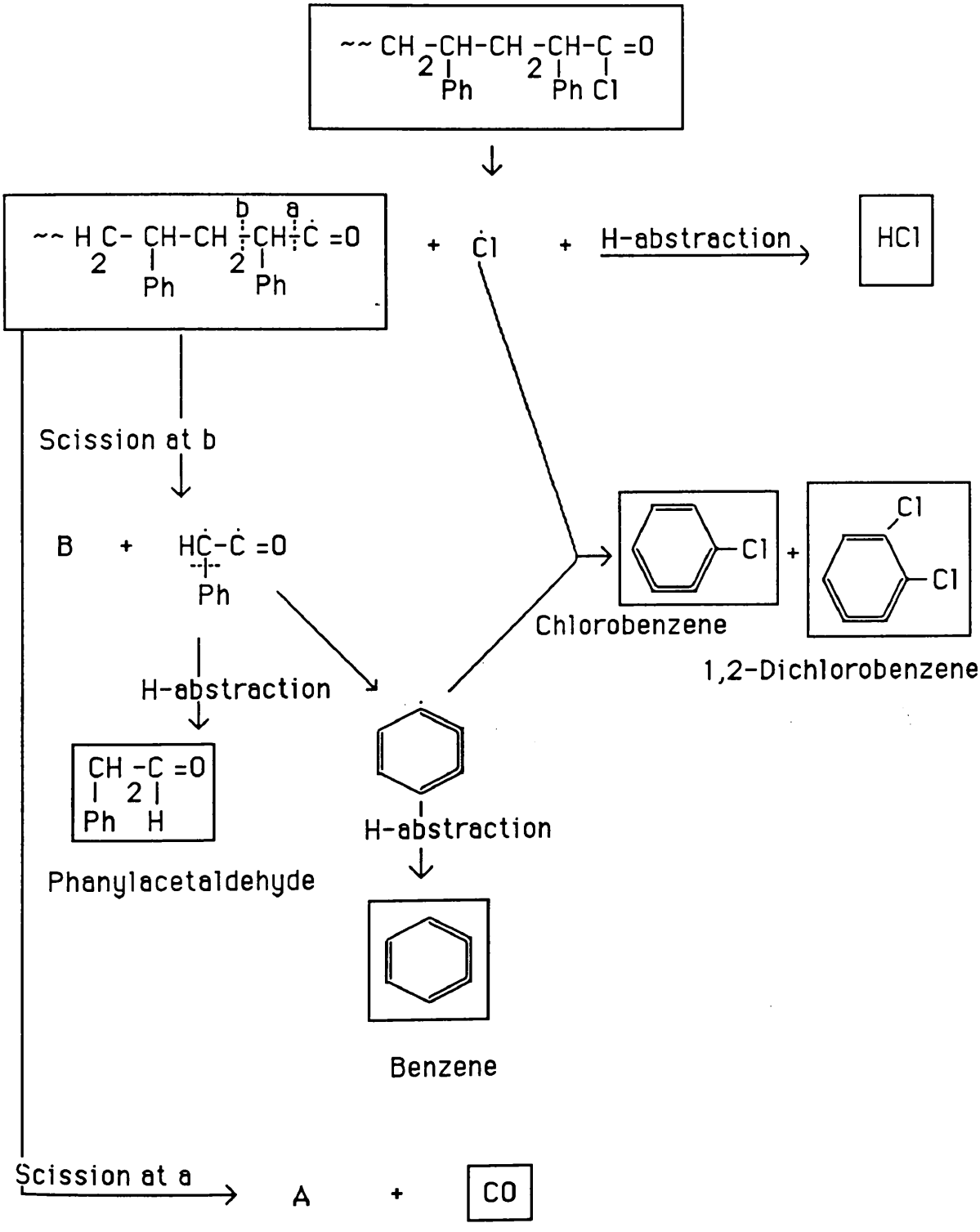
Scheme 1 Mechanism of.formation of Minor Products from Chain Ends in Degradation of Dihydroxyl-Terminated Polystyrene (HO -PS - OH).



Scheme 2 Mechanism of Formation of Minor Products from Chain Ends in Degradation of HO_2C-PS-CO_2H.



Scheme 3 Mechanism of Formation of Minor Products from Chain Ends in Degradation of ClOC-PS-COCl



CHAPTER SEVEN

THERMAL DEGRADATION OF METAL SALTS OF DICARBOXYL-TERMINATED POLYSTYRENE

The work described in this chapter concerns the thermal degradation of metal salts of bifunctional carboxyl-terminated polystyrene (HO_2C-PS-CO_2H) under programmed (10 ^oC/min) and isothermal heating conditions.

The main objectives were to examine the effect on stability and to elucidate the mechanism of thermal decomposition of the polymers, with particular interest in the initial stages of decomposition.

1. INTRODUCTION

Nothing has been published about the mechanism of decomposition of metal salts of dicarboxyl-terminated polystyrene, but over the past 30 years a number of systems containing inorganic elements in the main chain have been investigated, particularly for higher temperature applications.[93]

The development of materials containing salt groups has undergone explosive growth in recent years.[13,94] Polymeric structures encompassed by the field of ionic polymers are extremely varied, ranging from naturally occurring biopolymers to inorganic glasses and ceramics.[95]

A number of different backbones and pendant acid groups have been prepared by different workers.[95-99] Despite the considerable industrial and academic research effort which has been expended on ionomers, there is still a lack of general

agreement about the structure of polymers with ions in the backbone. Brown [11] has observed that when carboxylate polymers were neutralised by an appropriate cation such as zinc, the structure may be depicted schematically as;

$$\begin{array}{c} -COO^- \\ Zn^{2+} \\ -COO^- \end{array}$$

with the Zn^{2+} ion bridging two carboxylate ions.

Otocka et al.[100] modified the picture for monovalent cations.which produced largely the same effects as divalent cations such as zinc, by representing the structure of the former schematically as;

$$\begin{array}{c} M^{+-}OOC- \\ -COO^{-+}M \end{array}$$

Such a concept recognises the probability that in the media of such low dielectric constant, salt groups would be present as contact ion pairs.

1.1. Polymerisation

The linear polymers containing sodium, calcium and zinc ions were prepared from carboxyl-terminated polystyrene as described in Chapter Three.

2. THERMAL DEGRADATION

Thermal behaviour of these materials has been studied by using TVA, TG and DTA techniques, with examination of degradation products in the case of the TVA experiments.

2.1. Programmed Heating Experiments

2.1.1. Thermal Volatilisation Analysis Curves

The sample size was 50 mg for each polymer. The polymer samples were degraded to 500 ^{o}C at a heating rate of 10 ^{o}C/min, under normal conditions of TVA as described in Chapter Two. The TVA traces for NaO_2C-PS-CO_2Na, ~~O_2C-PS-CO_2-Ca~~ and ~~O_2C-PS-CO_2-Zn~~ are reproduced in Fig. 7.1(a,b,c), respectively.

No volatile product is given off below 340 ^{o}C which indicates that these polymers contain no water. In the case of ~~O_2C-PS-CO_2-Zn~~, there is a greater amount of non-condensable gases evolved, although the amounts are small in all three cases. In each case the TVA traces consist of a single peak, with T_{max} at 420^{o}, 417^{o} and 416 ^{o}C, respectively for the sodium, calcium and zinc salts. The difference in T_{max} temperatures is negligible. This is the same T_{max} as normal polystyrene and probably reflects the fact that the main reaction is the same in all three polymers.

Further examination of the TVA traces shows the presence of high boiling material indicated by the limiting rate effect[28] in the -45 ^{o}C trace, which is typical of the main product, styrene. It is also apparent that the T_{max} values in the -100^{o} and -196 ^{o}C traces occur at lower temperature than that of the main peak (0^{o} trace), indicating two degradation processes which overlap in temperature range, with that giving the very volatile products occurring predominantly in the lower temperature part of the decomposition.

2.1.2. Product Analysis

The products of degradation of the polymers to 500 ^{o}C under TVA conditions

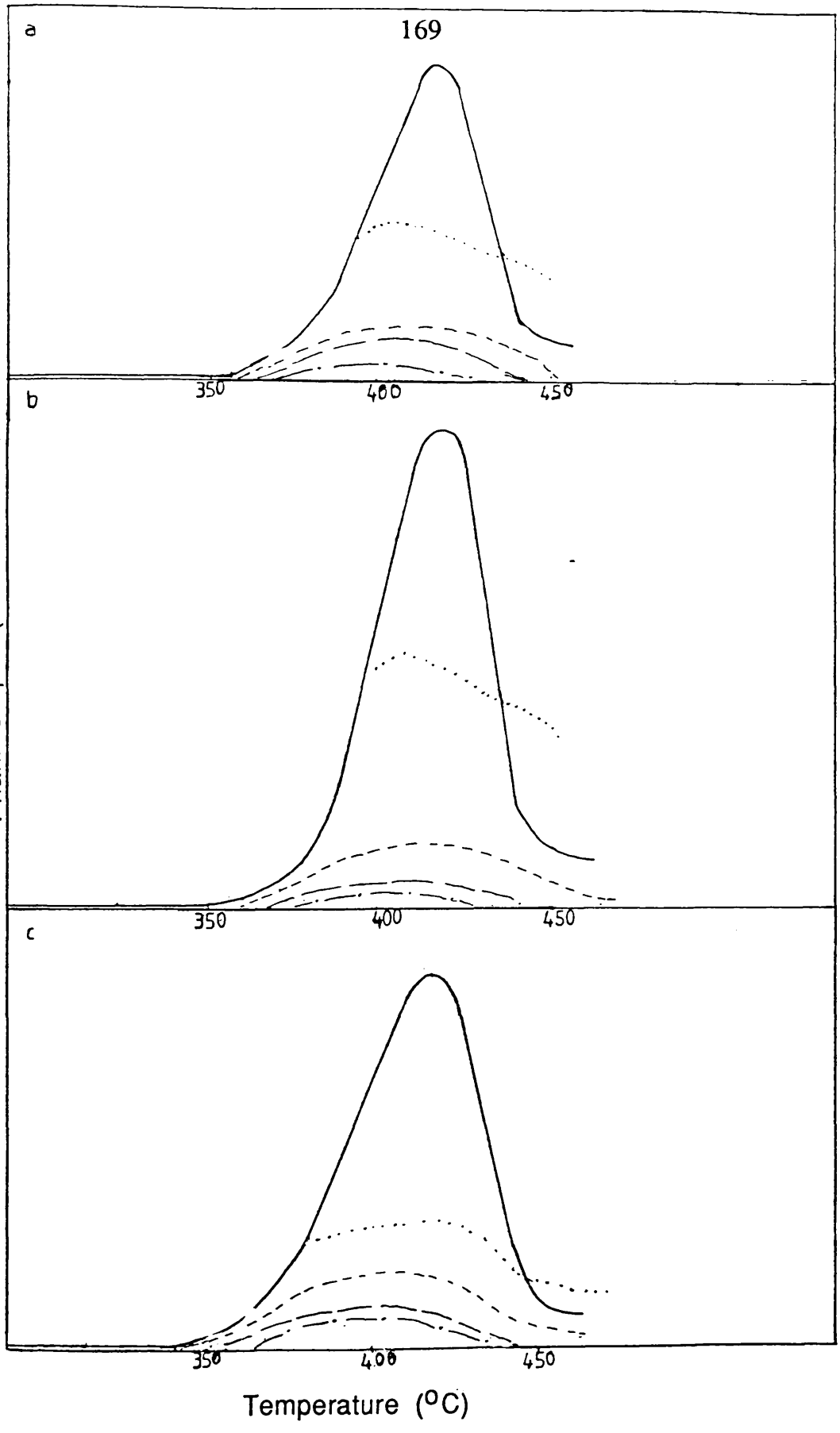


Fig. 7.1. TVA curves (vacuum, heating rate 10 °C/min) for metal salts of dicarboxyl-terminated Polystyrene. (a) Na (b) Ca (c) Zn.

Keys: ___ 0°, ...-45°, - - - -75°, __ __ -100°, __ . __ -196 °C.

were investigated by the techniques already described in Chapter Four. These were examined as four main fractions, consisting of involatile residue, cold ring fraction, condensable volatile fraction and non-condensable gases.

2.1.3. Subambient Thermal Volatilisation Analysis

SATVA traces for the sodium, calcium and zinc salt polymers are reproduced in Figs. 7.2, 7.3 and 7.4, respectively. Products were collected in three fractions for the sodium and calcium salts and five fractions for the zinc salt. Assignments of materials present, based on IR and GC-MS investigation, are shown in Table 7.1 and 7.2.

2.1.4. Residue

The black residues from degradation of the polymers to 500 ^{o}C were examined by IR spectroscopy. The main peaks found in the residue spectra were ;

a; Sodium salt
2910 (w), 1440 (b), 870 (m), 700-695 (m) cm^{-1}

b; Calcium salt
2505 (w), 1800 (w), 1450 (b), 880 (s), 720 (m) cm^{-1}

c; Zinc salt
3120-2910 (b), 1590 (b), 1450 (m), 750 (m), 700 (s) cm^{-1}
s = small, m = medium, b = broad, w = weak

By comparison with standard spectra, it is concluded that in all three cases the main constituents of the involatile materials are the respective metal carbonates and metal oxide. The IR spectra of the residues are shown in Fig. 7.5. A broad

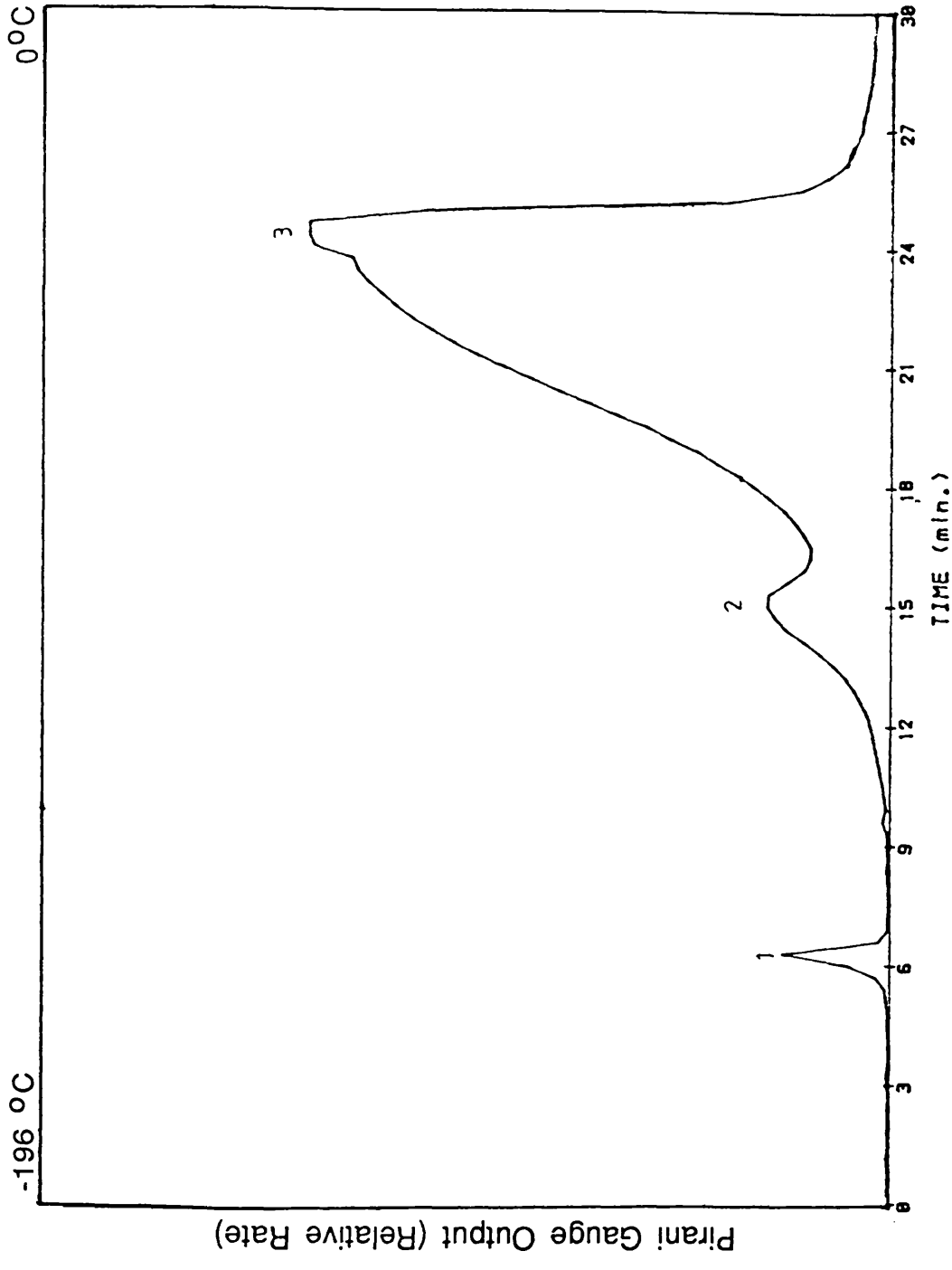


Fig. 7.2. SATVA curve of condensable volatile product fraction from degradation to 500 °C under TVA conditions of sodium salt of dicarboxyl-terminated Polystyrene. Products were collected in three fractions as indicated .

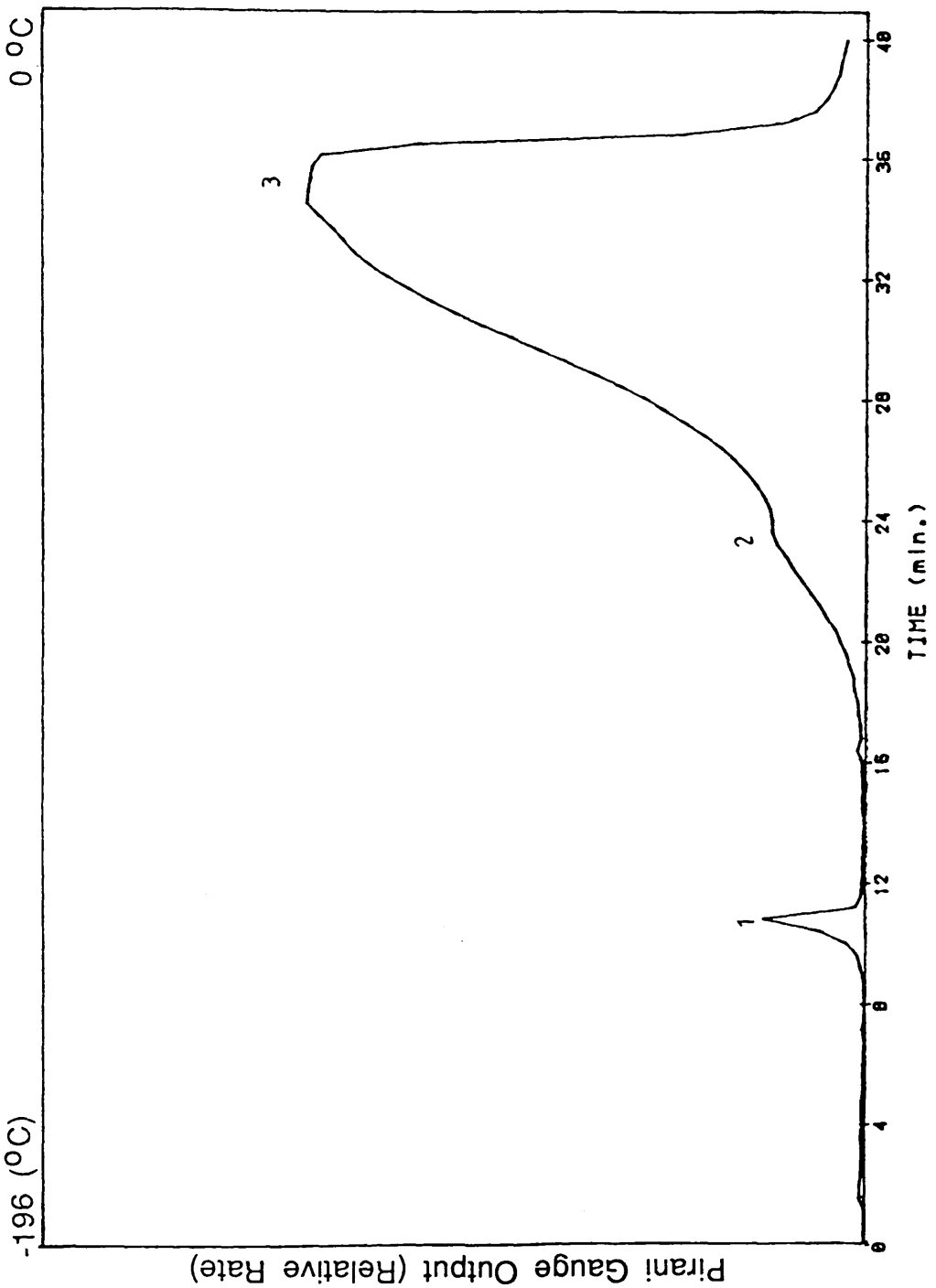


Fig. 7.3. SATVA curve of condensable volatile product fraction from degradation to 500 °C under TVA conditions of calcium salt of dicarboxyl-terminated Polystyrene. Products were collected in three fractions as indicated .

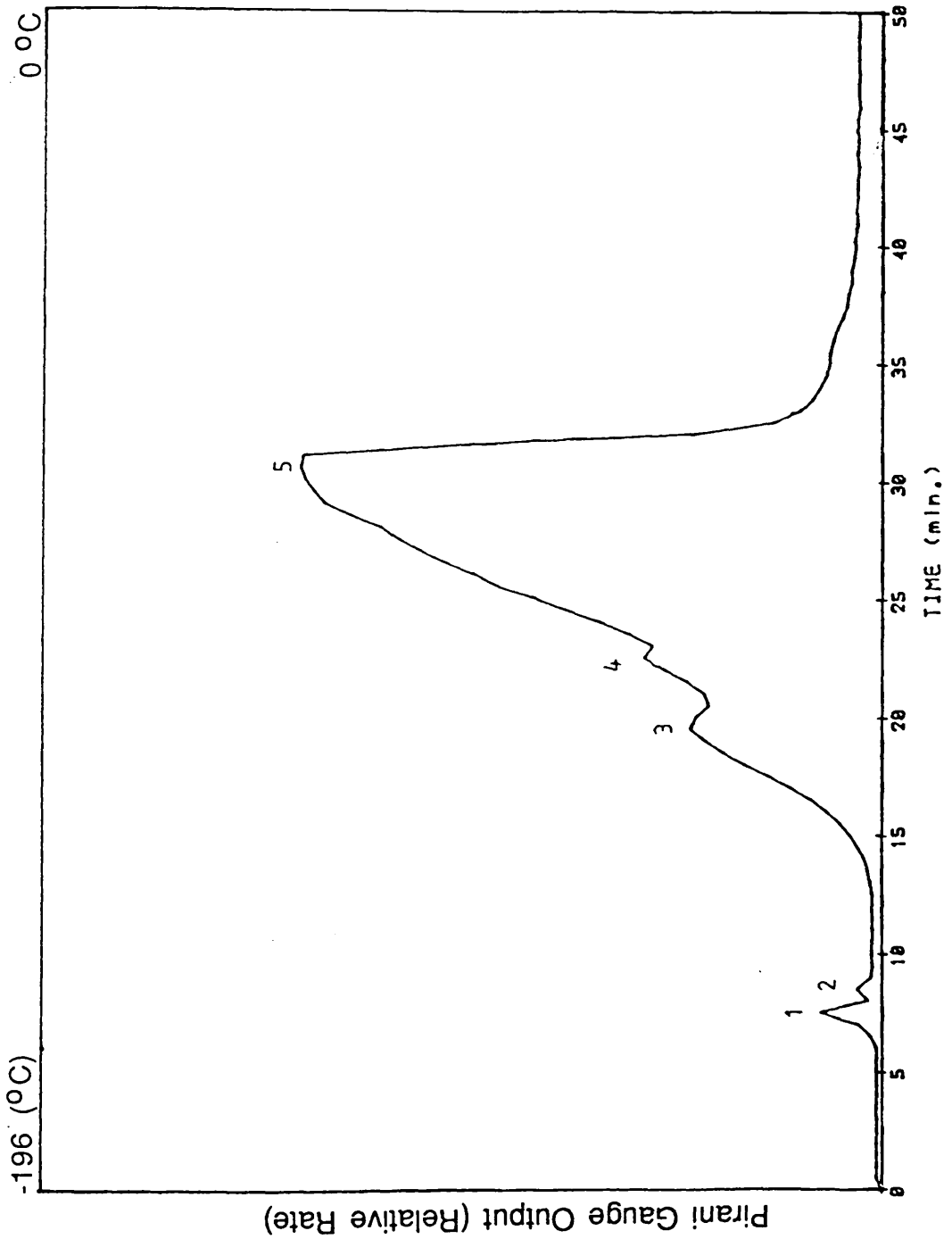
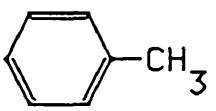
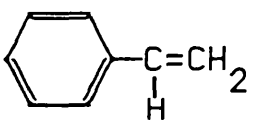
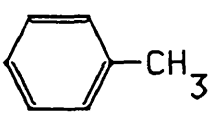
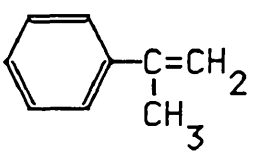
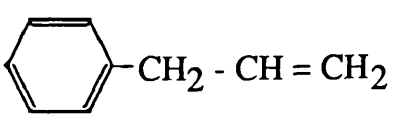
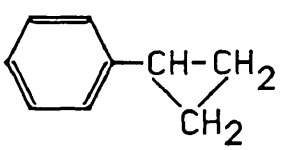


Fig. 7.4. SATVA curve of condensable volatile product fraction from degradation to 500 °C under TVA conditions of zinc salt of dicarboxyl-terminated Polystyrene. Products were collected in five fractions as indicated .

Table 7.1 Assignment of Volatile Products of Na and Ca Salt Polymer Samples Degraded to 500 °C in the TVA System Under Vacuum Using Programmed Heating and Separated by SATVA. (MS ion peaks in order of abundance)

Peak No.	Compounds	IR	MS
1	CO_2	2340, 669 cm^{-1}	44,28,16
2		3060,3040,2950,	78,52,39
		730,690,670 cm^{-1}	91,92,39,65
3		3090-3010,2950-	104,105,102,27
		2850,2000-1800,	91,92,39
		1695,1630,1600,	118,117,103,78,51
		1580,1500,1450,	117,118,103,78,
		1410,1205,1090,	118,117,91,115

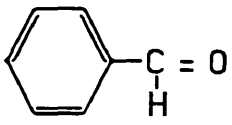
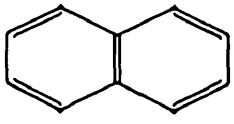
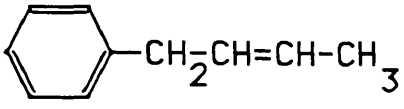
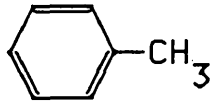
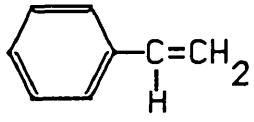
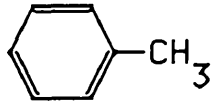
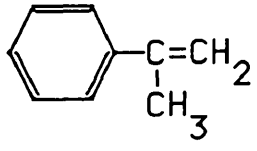
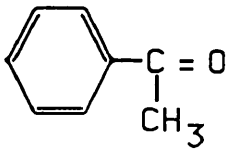
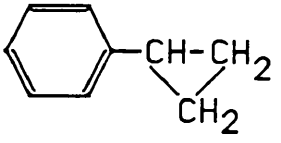
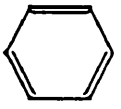
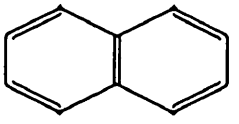
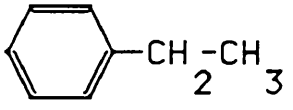
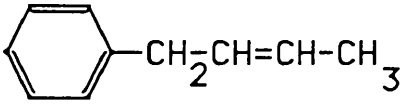
	1020,990,910,	77,105,106,51
	780,735 cm^{-1}	128,127,129,51
		91,132,39,65

Table 7.2 Assignment of Volatile Products of Zn Salt Polymer Sample Degraded to 500 ^{o}C in the TVA System Under Vacuum Using Programmed Heating and Separated by SATVA. (MS ion peaks in order of abundance.)

Peak No	Compounds	IR	MS
1	CO_2	2340,669 cm^{-1}	44,28,16
2	HCOH	2780,1750,1720 1280,1160 cm^{-1}	
3		2980,2870,1460 1070,910 cm^{-1}	
4		3060,3024,2940,	78,52,39
		730,690,670 cm^{-1}	91,92,39,65
5		3090-3010,2950,	104,105,103,27
		2860,2000-1800,	91,92,39
		1690,1630,1600,	118,117,103,78,115

	1580,1500,1450,	105,77,51,120,50
	1410,1390-1290,	118,117,91,38
	1200,1090,1020,	78,52,39
	990,789,735,	128,127,129,51
	700cm^{-1}	91,106,105,77
		91,132,39,65

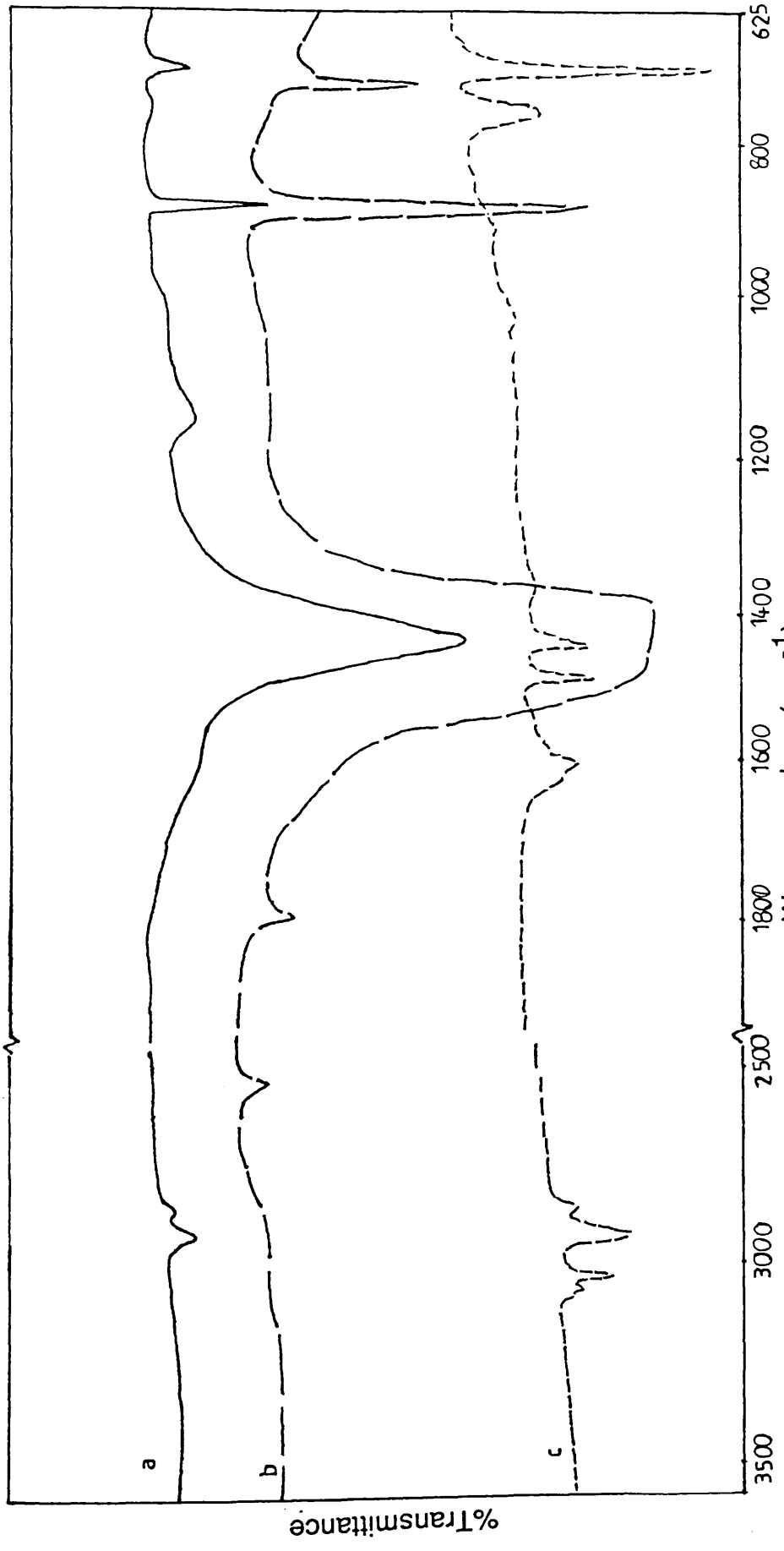


Fig. 7.5. Infrared spectra of the involatile fraction from degradation of metal salts of dicarboxyl-terminated Polystyrene to 500 °C under TVA conditions. (a) NaO_2C-PS-CO_2Na, (b) ~~O_2C-PS-CO_2-Ca~~, (c) ~~O_2C-PS-CO_2-Zn~~

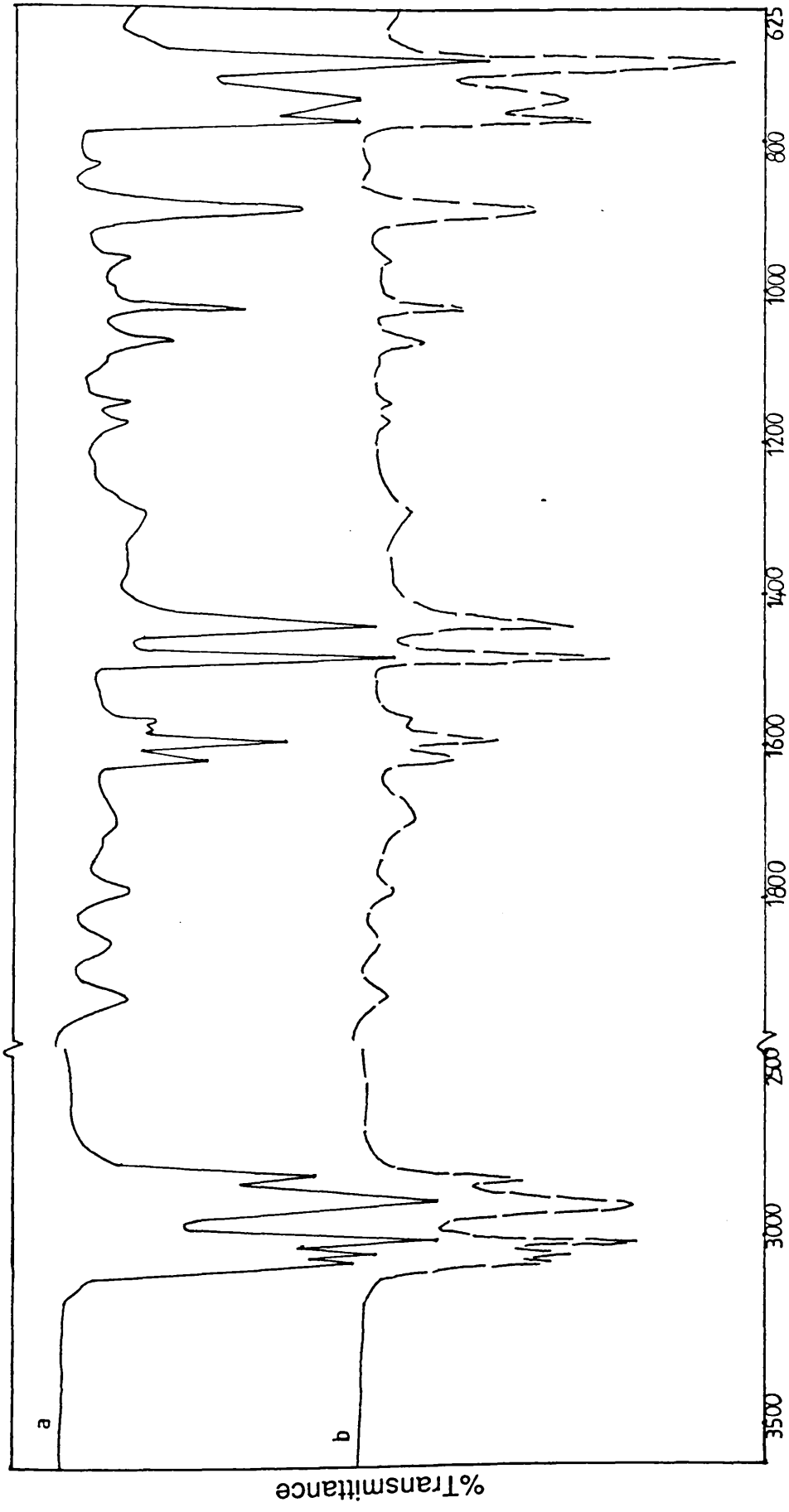


Fig. 7.6. Infrared spectra of the CRF from degradation of metal salts of dicarboxyl-terminated Polystyrene to 500 ^{o}C under TVA conditions.

(a) NaO_2C-PS-CO_2Na, (b) ~~O_2C-PS-CO_2-Ca~~.

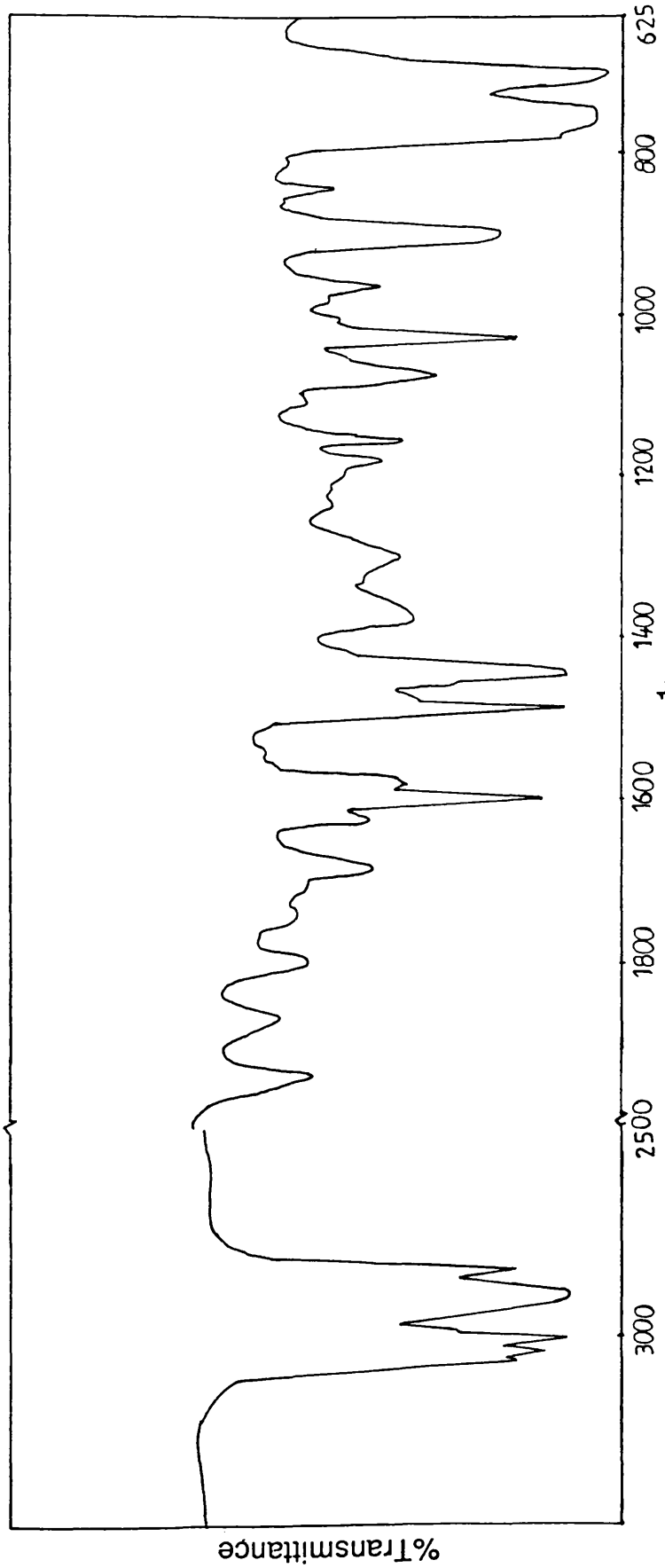


Fig. 7.7. Infrared spectrum of CRF from degradation of ~~O_2C-PS-CO_2-Zn~ to 500 °C under TVA conditions.

Table 7.3 Product Fractions (wt%) in the Degradation of Sodium, Calcium and Zinc salts of Dicarboxly-Terminated Polystyrene to 500 ^{o}C Under TVA Conditions.

Fractions	NaO_2C-PS-CO_2Na	~O_2C-PS-CO_2Ca~	~O_2C-PS-CO_2Zn~
Total volatile products	55.50	54.50	56.01
Cold ring fraction	39.50	38.50	42.06
Residue	4.0	7.0	2.0

2.1.6. Gaseous Volatile Products

Infrared spectroscopic analysis of the non-condensable volatile material established the presence of carbon monoxide.

The condensable gaseous products identified by infrared spectroscopy and mass spectrometry, consisted of carbon dioxide from all three polymers and formaldehyde only in the case of Zn polymer.

2.1.7. Liquid Fraction of Volatile Products

The weight percentage of the less volatile condensable liquid fraction was more than fifty percent. Product analysis of the liquid fractions, separated by SATVA, were carried out using IR and MS.

These spectra were similar to the IR spectrum of styrene, the only difference being the presence of a band at 1690 cm^{-1} due to carbonyl absorption.

Mass spectrometric analysis confirms styrene as a principal product in the volatile liquid fraction together with small amounts of toluene, benzene and α-methylstyrene and traces of other materials.

All the products detected from the degradation of sodium, calcium and zinc metal salts of dicarboxyl-terminated polystyrene under programmed heating to 500 ^{o}C are listed in Tables 7.6, 7.7 and 7.8, respectively.

2.1.8. Thermogravimetry

TG and DTG curves obtained in the degradation of the three metal containing polymers, reproduced in Figs. 7.8, 7.9 and 7.10, show a single stage of weight

Table 7.4 Products Identified in the Cold Ring Fraction from Degradation of NaO_2C-PS-CO_2Na Under Normal TVA Conditions to 500 °C.

Products	Name	m/e
H_2C(Ph)-CH_2-CH_2(Ph)	1,3-diphenyl propane	196
H_2C=C(Ph)-CH_2-CH_2(Ph)	styrene dimer	208
H_2C=C(Ph)-CH_2-CH(Ph)-CH_3	dimer with extra methyl group	222
H_2C=C(Ph)-CH_2-CH(Ph)-C(H)=O	dimer with extra aldehyde group	235
H_2C=C(Ph)-CH_2-CH(Ph)-CH_2-CH_2(Ph)	trimer	312
H_2C=C(Ph)-CH_2-CH(Ph)-CH_2-CH(Ph)-CH_3	trimer with extra methyl group	326
H_2C=C(Ph)-CH_2-CH(Ph)-CH_2-CH(Ph)-C(OH)=O	trimer with carboxyl group	355
H_2C=C(Ph)-(CH_2-CH(Ph))$_2$-CH_2-CH_2(Ph)	tetramer	412
H_2C=C(Ph)-(CH_2-CH(Ph))$_3$-CH_2-CH_2(Ph)	pentamer	520

Table 7.5 Products Identified in the Cold Ring Fraction from Degradation of ~O_2C-PS-CO_2-Zn~ Under Normal TVA Conditions to 500 °C.

Products	Name	m/e
H_3C-COOCO-CH_2 (Ph)	mixed anhydride of acetic and phenylacetic acids	178
H_2C(Ph)-COOCO-CH(Ph)-CH_3	mixed anhydride of phenyl acetic and 2-phenylpropanoic acids	268
H_2C=C(Ph)-COOCO-CH(Ph)-CH_3	mixed anhydride of 2-phenylacrylic and 2-phenyl propanoic acids	280
H_2C=C(Ph)-CH_2-CH_2(Ph)	styrene dimer	208
H_2C=C(Ph)-CH_2-CH(Ph)-CH_3	dimer with extra methyl group	222
H_2C=C(Ph)-CH_2-CH(Ph)-C(H)=O	dimer with aldehyde group	236
H_2C=C(Ph)-CH_2-CH(Ph)-CH_2-CH_2(Ph)	trimer	312
H_2C=C(Ph)-CH_2-CH(Ph)-CH_2-CH(Ph)-CH_3	trimer with extra methyl group	326

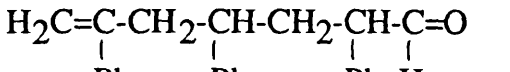
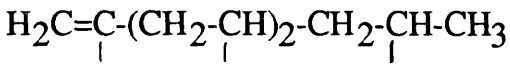
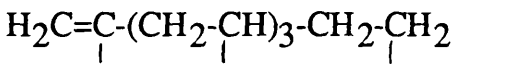
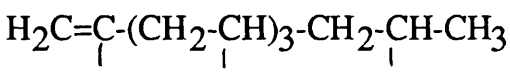
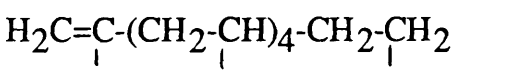
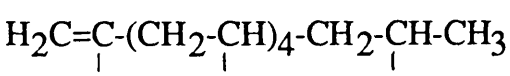
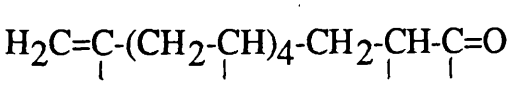
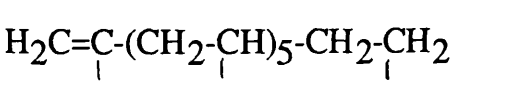
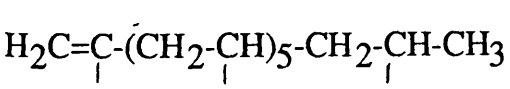
	trimer with aldehyde group	340
	tetramer with extra methyl group	430
	pentamer	520
	pentamer with extra methyl group	534
	hexamer	624
	hexamer with extra methyl group	638
	hexamer with aldehyde group	652
	heptamer	728
	heptamer with extra methyl group	742

Table 7.6 Products of Degradation of NaO_2C-PS-CO_2Na to 500 °C at 10°C/min Under TVA Conditions.

Non-condensable product at -196 °C	Condensable volatile products at -196 °C		CRF	Residue
Gases	Gases	Liquid Fraction		
IR, MS	IR, MS	IR, MS, GC-MS	IR,TLC,MS	IR
CO	CO_2 Toluene Benzene	Styrene ∝-methyl styrene Toluene Benzene Phenyl acetic acid Phenylacet-aldehyde Allylbenzene Cyclopropyl benzene Benzaldehyde Naphthalene	Dimer, Trimer and Short chain fragments containing carbonyl group.	Sodium carbonate as a major Product

Table 7.7 Products of Degradation of ~~O_2C-PS-CO_2-Ca~~ to 500 °C at 10°C/min Under TVA Conditions.

Non-condensable product at -196 °C	Condensable volatile products at -196 °C		CRF	Residue
	Gases	Liquid Fraction		
IR	IR,MS	IR,MS,GC-MS	IR,TLC,MS	IR
CO	CO_2 Toluene	Styrene Toluene ∝-methyl styrene Allylbenzene 4-phenyl-1-butene Phenylprop-analdehyde Naphthalene Benzaldehyde Phenyl acetaldehyde	Dimer Trimer Tetramer Dimer and trimer with extra methyl group Dimer, trimer and pentamer containing carbonyl group.	Mainly calcium carbonate and trace amount of calcium oxide.

Table 7.8 Products of Degradation of ~~O_2C-PS-CO_2-Zn~~ to 500 ^oC at 10^oC/min under TVA Conditions.

Non-condensable product at -196 ^oC	Condensable volatile products at -196 ^oC		CRF	Residue
	Gases	Liquid Fraction		
IR,MS	IR,MS	IR,MS,GC-MS	IR,MS	IR
CO CH_4	CO_2 HCOH THF Benzene Toluene	Styrene Toluene ∝-methyl styrene Ethylbenzene Phenylprop-ionaldehyde Acetophenone Phenyl acetaldehyde Naphthalene Benzene	Dimer and methyl dimer as a major product Small amount of anhyride	Zinc oxide as a major product.

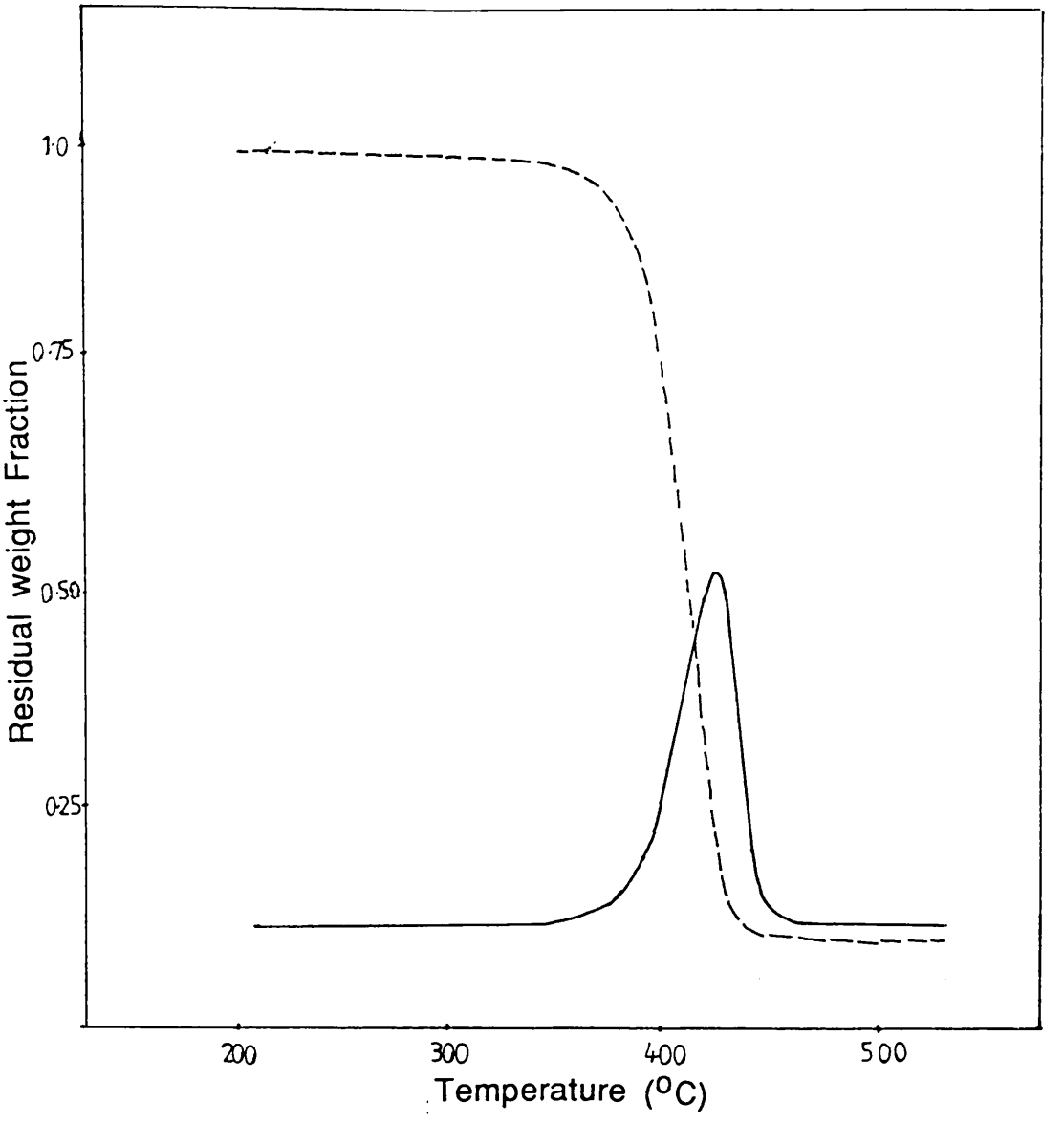


Fig. 7.8. TG and DTG curves for sodium salt of dicarboxyl-terminated Polystyrene under dynamic nitrogen atmosphere, heating rate 10 °C/min. _ _ _ TG, ___ DTG

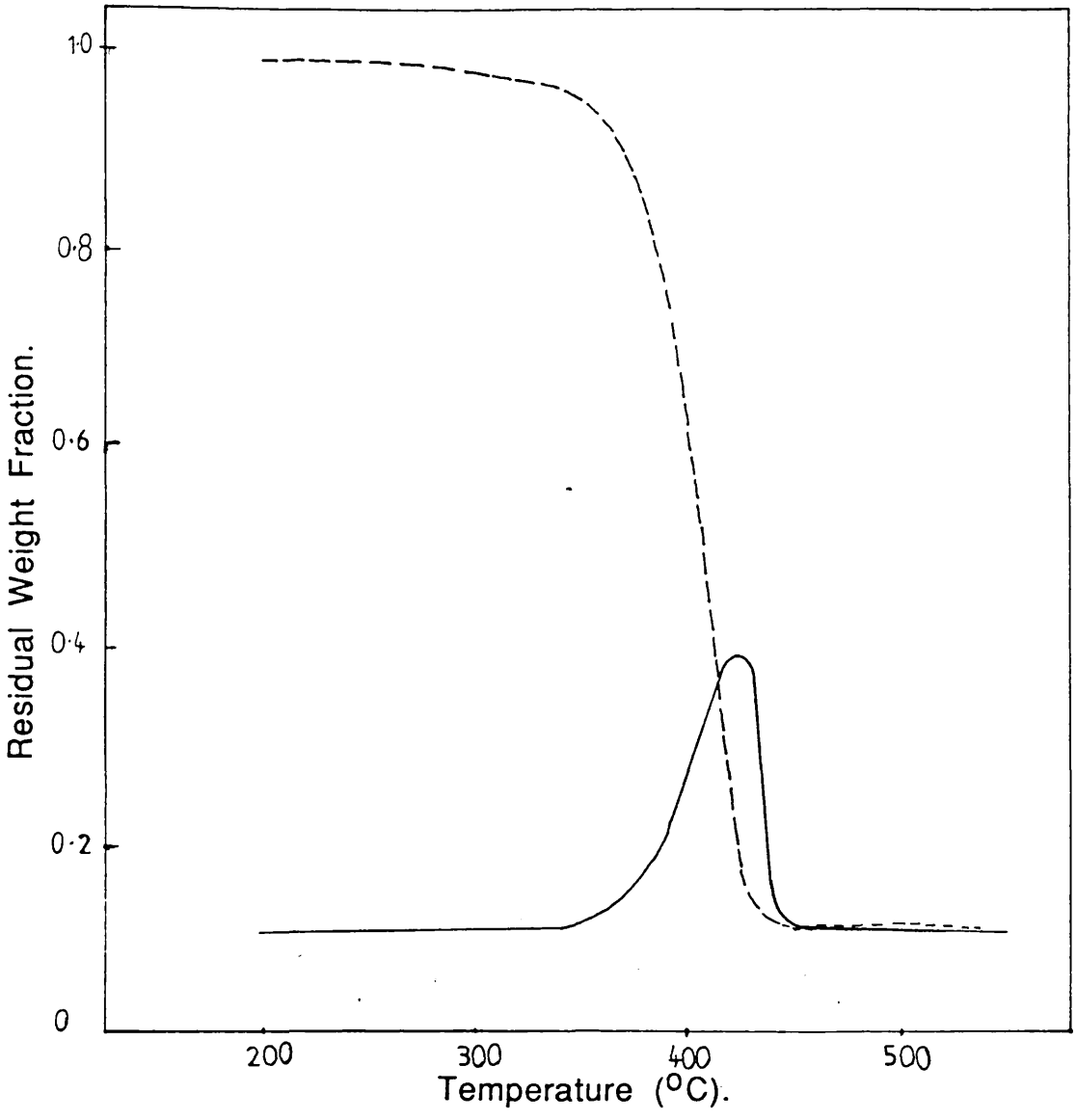


Fig. 7.9. TG and DTG curves (dynamic nitrogen atmosphere, heating rate (10°C/min) for calcium salt of dicarboxyl-terminated Polystyrene. Keys: _ _ _ TG, ___ DTG.

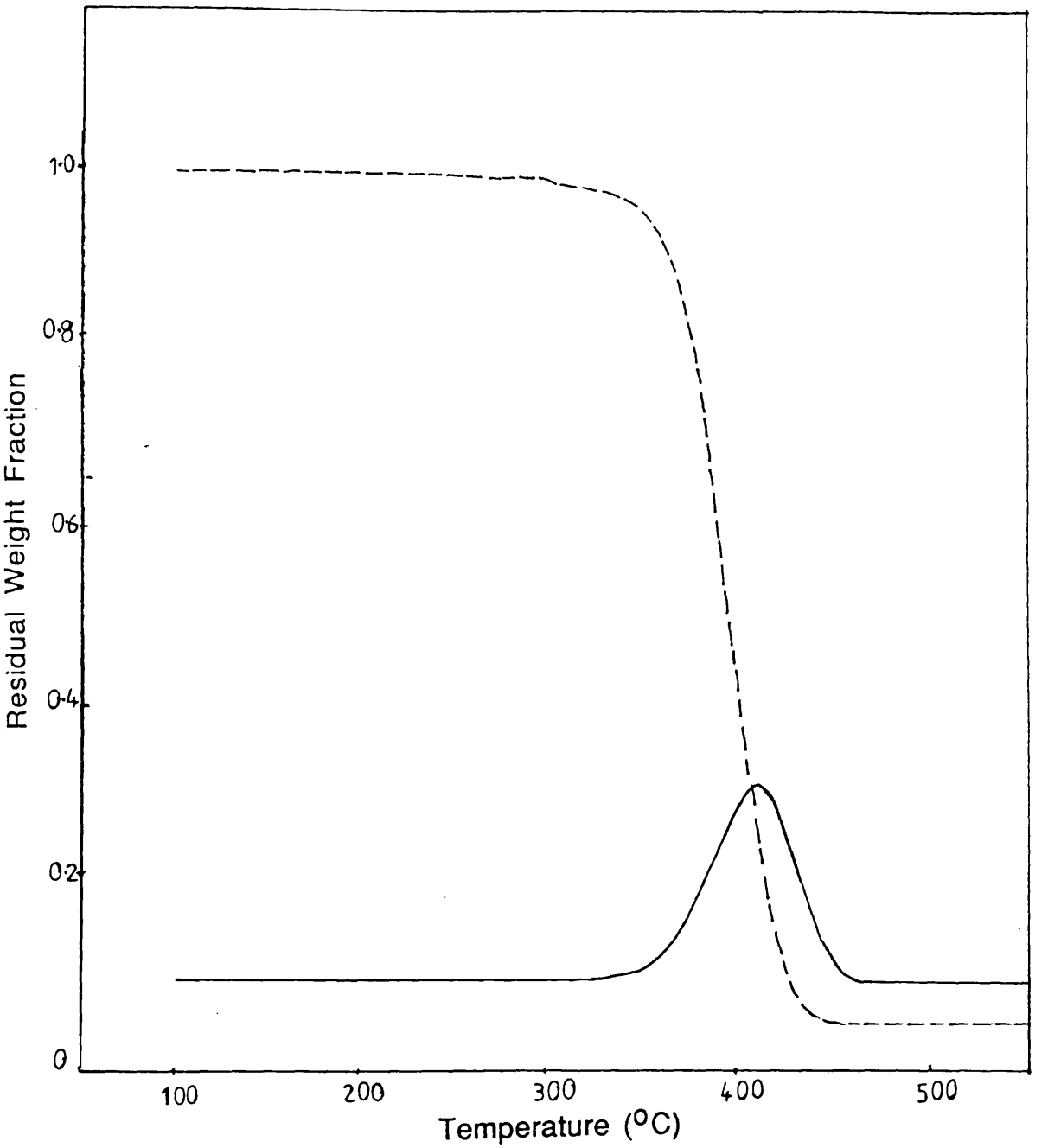


Fig. 7.10. TG and DTG curves for zinc salt of dicarboxyl-terminated Polystyrene under dynamic nitrogen atmosphere, herating rate 10 °C/min.

Keys: _ _ _ TG, ___ DTG.

loss which begins at a lower temperature in the case of Zn salt than for the Na and Ca salts. The main decomposition, leaving metal carbonate and metal oxides, is observed above 400 ^{o}C. The total weight losses near 500 ^{o}C for Na, Ca and Zn are 93, 91 and 95%, respectively. The main features are summarised in Table 7.9.

2.1.9. Differential Thermal Analysis

The thermal stability of the polymers was also examined by the DTA technique in range of 25^{o}-500 ^{o}C under dynamic nitrogen. The DTA curves in Fig. 7.11 show the main step of decomposition of polymer salts occurring between 400^{o}-450 ^{o}C.

In the case of sodium salt, the DTA curve shows partial degradation as an endothermic small shoulder at 393 ^{o}C, followed by the main endotherm at 430^{o}C. In the Ca salt the DTA curve shows a broad endothermic shoulder at about 392 ^{o}C, followed by the main endotherm. There is no clear defined endothermic shoulder in the case of the Zn salt, although endothermic drift occurs between 250^{o} and 400 ^{o}C.

The features revealed by DTA are consistent with the pattern of behaviour shown in TG and TVA, indicating a degradation process just before the main stage of decomposition.

2.2. ISOTHERMAL HEATING EXPERIMENTS

In this investigation, the metal containing dicarboxylate polystyrene samples were degraded isothermally under nitrogen at 340 ^{o}C in the thermobalance and also at 300^{o}, 350^{o} and 420 ^{o}C under normal TVA conditions. These temperatures were chosen to cover the normal temperature region of decomposition of polystyrene.

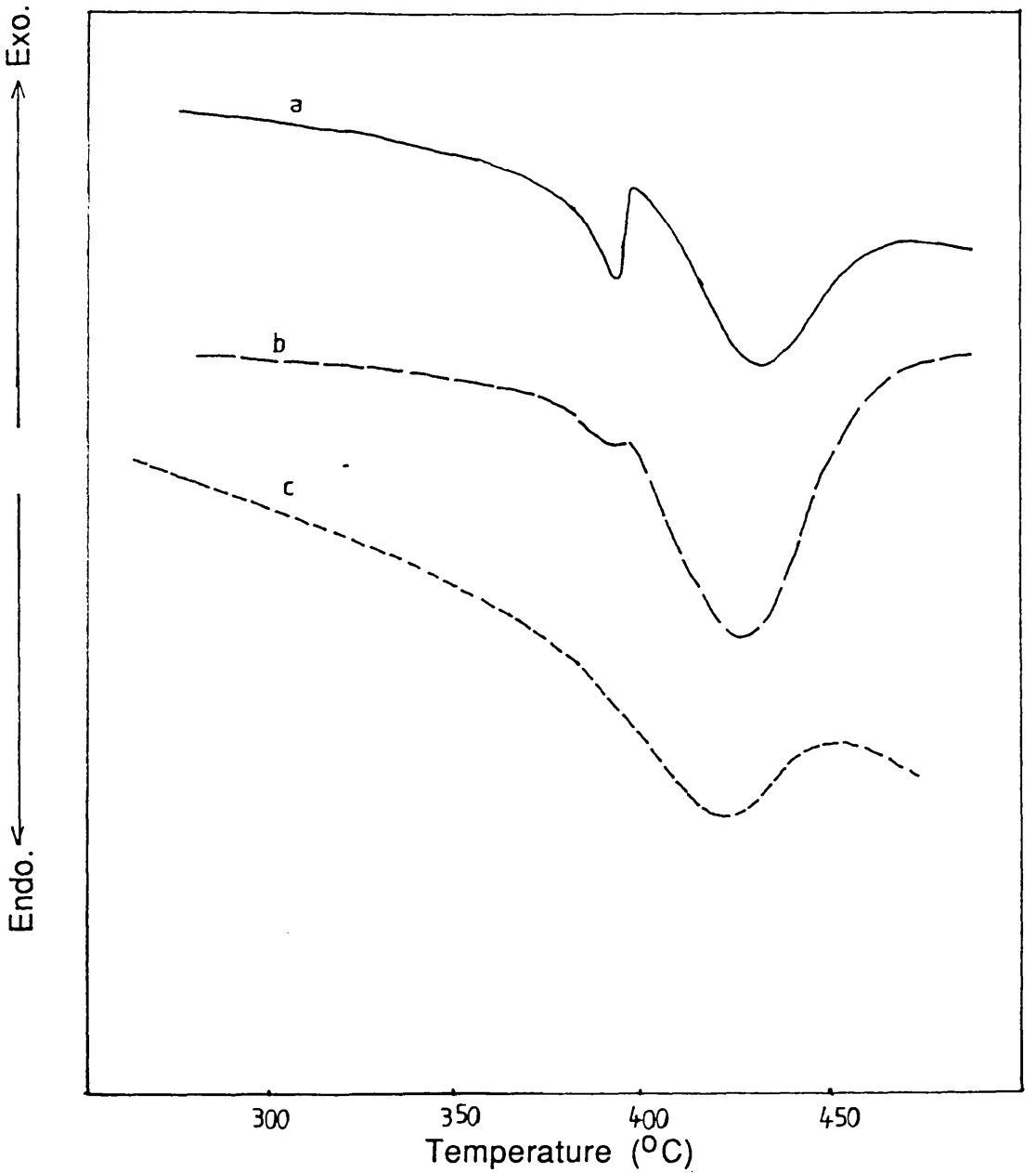


Fig. 7.11. DTA curves for metal salts of dicarboxyl-terminated Polystyrene under nitrogen atmosphere, heating rate 10 °C/min. Keys: (a) NaO_2C-PS-CO_2Na, (b) ~~O_2C-PS-CO_2-Ca~~, (c) ~~O_2C-PS-CO_2-Zn~~.

Table 7.9 TG and DTG Data for Metal Salts of Dicarboxyl-Terminated Polystyrene. Dynamic Nitrogen Atmosphere, Heating Rate 10 °C/min to 500 °C.

Polymer	TG		Wt% residue at ~ 500 °C	DTG peak temp., °C
	T1% °C	T50% °C		
NaO_2C-PS-CO_2Na	350	400	7.0	428
~O_2C-PS-CO_2-Ca~	345	397	9.0	422
~O_2C-PS-CO_2-Zn~	340	390	5.0	420

2.2.1. Thermogravimetry

The isothermal TG traces for all three polymer samples at 340 ^{o}C under nitrogen are shown in Fig. 7.12. These traces indicate that percentage weight loss at any time decreases in the series Zn salt, Ca salt and Na salt. The weight losses are 96, 92 and 83% for the Zn, Ca and Na salts, respectively.

2.2.2. Isothermal Heating Under TVA Conditions

2.2.2.1. Isothermal Heating at 300 ^{o}C

150 mg of each polymer sample (Na, Ca and Zn salts) was degraded isothermally at 300 ^{o}C under TVA conditions. The total condensable volatile products were collected as liquid fractions. Product analysis was carried out using the same experimental approach already applied in programmed experiments.

2.2.2.1a. Condensable volatile products

Volatile products were analysed by GC-MS. The mass spectrometry data were consistent with the presence of styrene as the major product, with toluene and -methylstyrene as other significant products. Some other minor products were also present. Allylbenzene was formed in the degradation of all three salt samples but methylindene was produced only in degradation of Ca and Zn salts. Naphthalene was also present in the products from all three polymers, as an impurity retained from the polymerisation.

2.2.2.1b. Cold ring fraction

The light brown cold ring fractions obtained in very small amount from isothermal degradation of three polymers at 300 ^{o}C were characterised by IR and

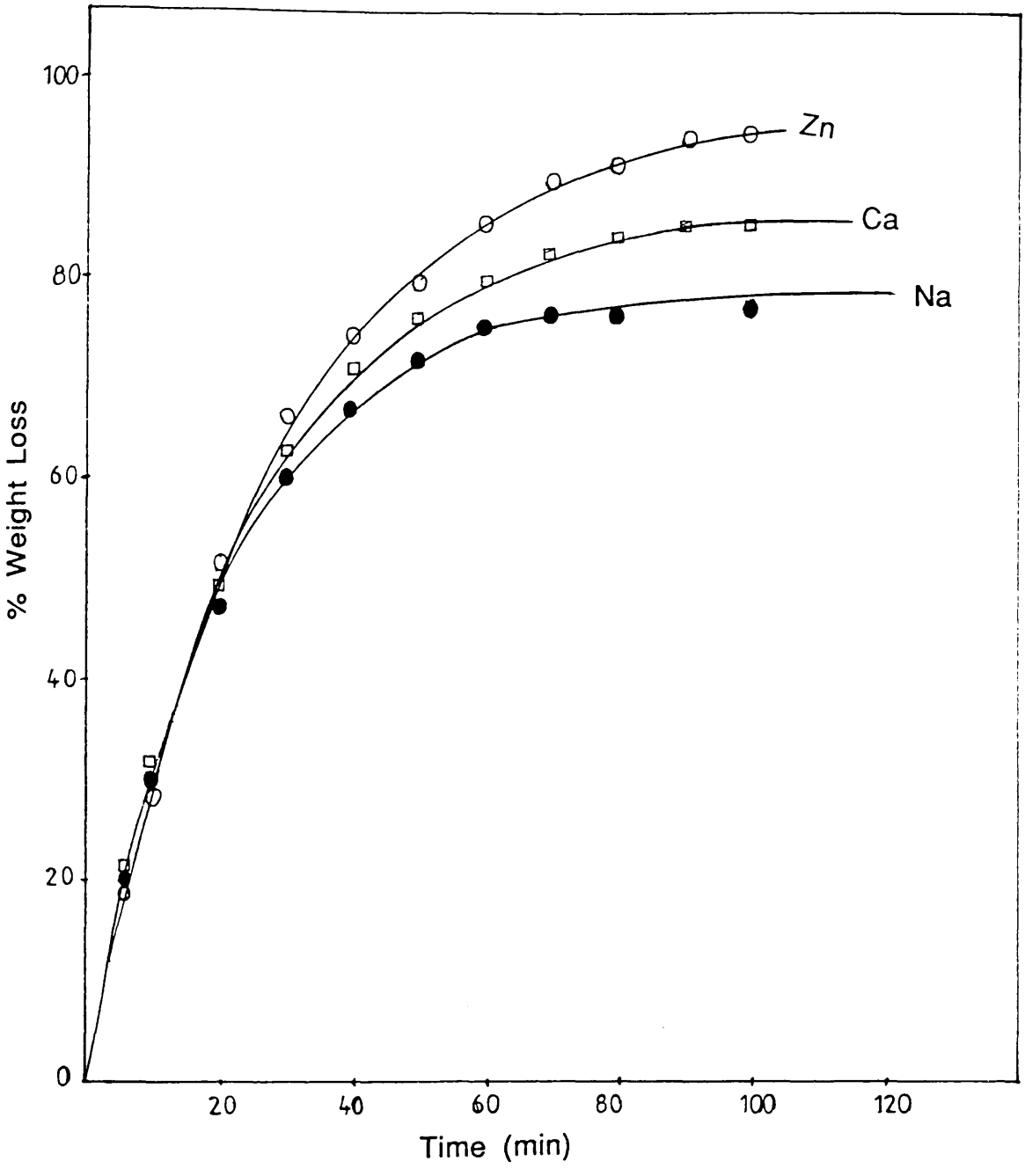


Fig. 7.12. The curves of weight loss vs time for metal salts of dicarboxyl-terminated Polystyrene, degraded isothermally at 340 ^{o}C under dynamic nitrogen, in the thermobalance.

MS. The infrared spectra and mass spectrometry data are consistent with the presence of short chain fragments such as dimer and dimer with an additional methyl group.

2.2.2.1c. Residue

The involatile residues at 300 ^{o}C were white materials with similar IR spectra to the original polymers. The IR spectra of all three residues contained bands at 1580-1520 cm^{-1}, which is due to asymetric and symmetric stretching modes of the carboxylate group.

2.2.2.2. Isothermal Heating at 350 ^{o}C

The residues from isothermal degradation at 300 ^{o}C were also degraded at 350 ^{o}C isothermally for half an hour and the degradation products were collected and separated by the SATVA technique.

2.2.2.2a. Condensables as gaseous products

Carbon dioxide (small amount), toluene and benzene (significant amount) were established by IR and MS as condensable gaseous products.

2.2.2.2b. Condensables as liquid products

The liquid products were analysed by IR spectroscopy. The IR spectra for all three liquid fractions showed an additional band at 1690 cm^{-1}, which was not present in the spectra of products from degradation at 300 ^{o}C.

The liquid fractions were collected by isothermal heating at this temperature (350^{o}C) for various times under TVA conditions and subjected to proton

resonance spectrometry for further investigation. The aromatic proton/aliphatic proton ratio for these liquid fractions was calculated and was plotted vs time as shown in Fig. 7.13. This suggests that the ratio increases with the passage of time but the increase is more rapid in the case of Zn salt liquid fraction in comparison with that of Ca salt.

2.2.2.2c. Cold ring fraction

Cold ring fractions were analysed by IR and MS methods. The IR spectra of those from the Na and Zn salts are shown in Fig. 7.14(a,b). These differ from the corresponding spectra obtained after heating at 300 ^{o}C only in the appearance of new absorption in the 1705-1690 cm^{-1} region, which is broad in the case of the product from the zinc salt.

2.2.2.2d. Residue

The IR spectra of the involatile residues from degradation of the Ca and Zn salts are reproduced in Fig. 7.15(a,b). IR spectra show some differences from the corresponding IR spectra in the experiment at 300 ^{o}C in the region of 1580-1550cm^{-1}.

2.2.2.3. Isothermal Heating at 420 ^{o}C

The residues from the experiments at 350 ^{o}C were further heated at 420 ^{o}C for 20 min.

2.2.2.3a. Condensables as liquid fraction

The liquid fractions were subjected to GC-MS investigation. Similar products were detected as at 350 ^{o}C.

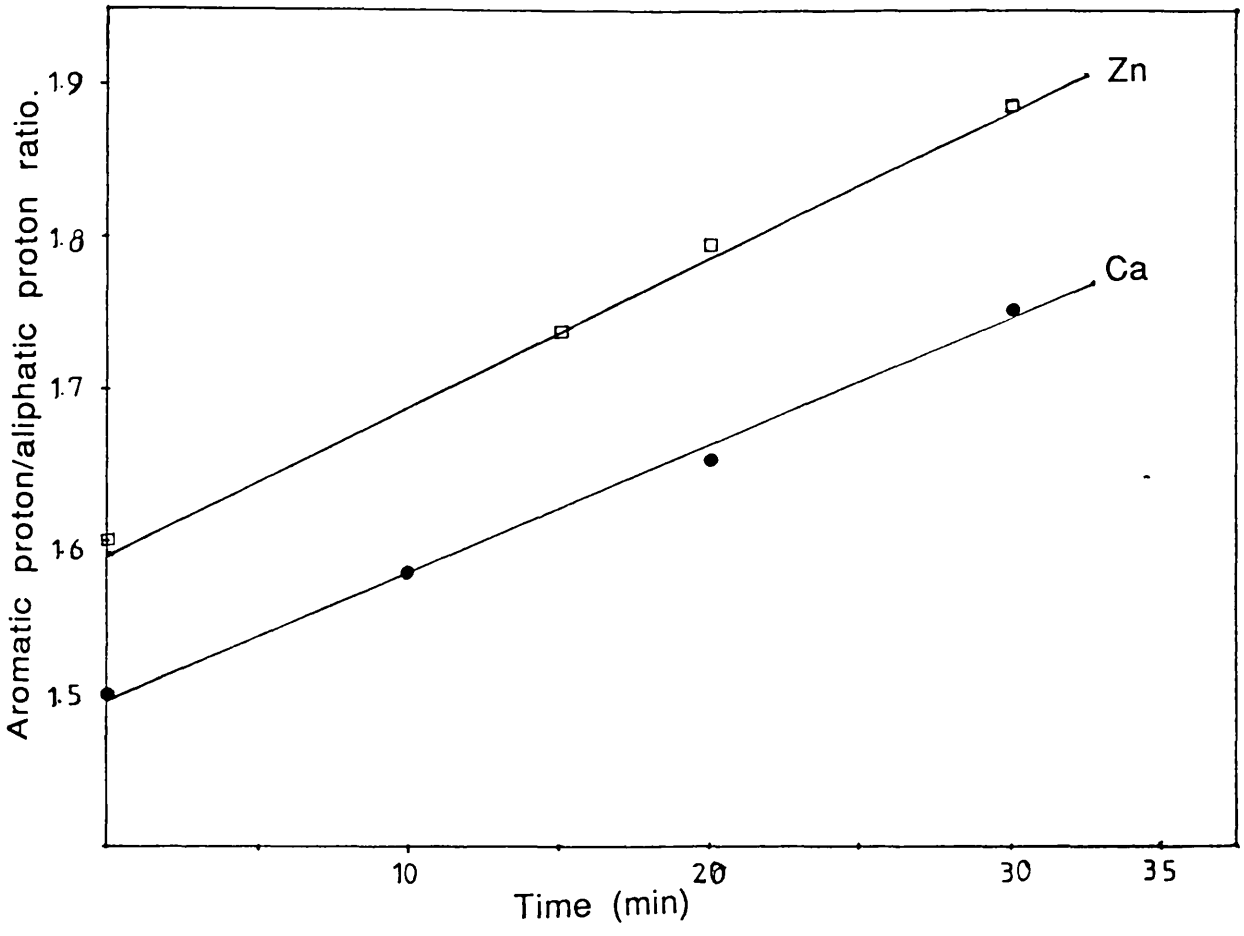


Fig. 7.13. Aromatic proton/aliphatic proton ratio in the liquid fraction vs time for zinc and calcium salts of dicarboxyl-terminated Polystyrene, degraded isothermally at 350 ^{o}C under TVA conditions.

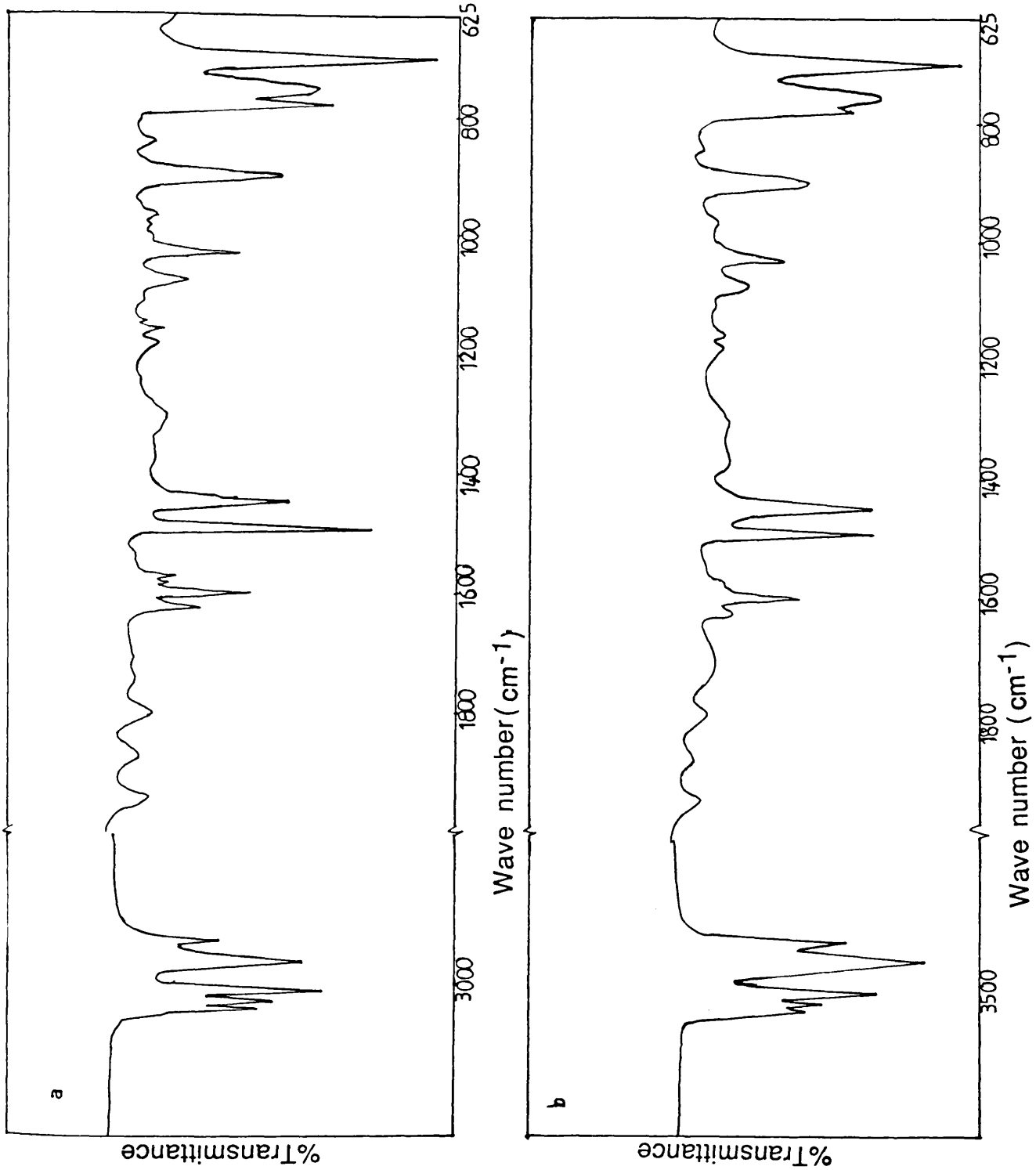


Fig. 7.14. Infrared spectra of the cold ring fraction from isothermal degradation, under TVA conditions at 300 ^{o}C for 20 min, of metal salts of dicarboxyl-terminated Polystyrene. (a) Na, (b) Zn.

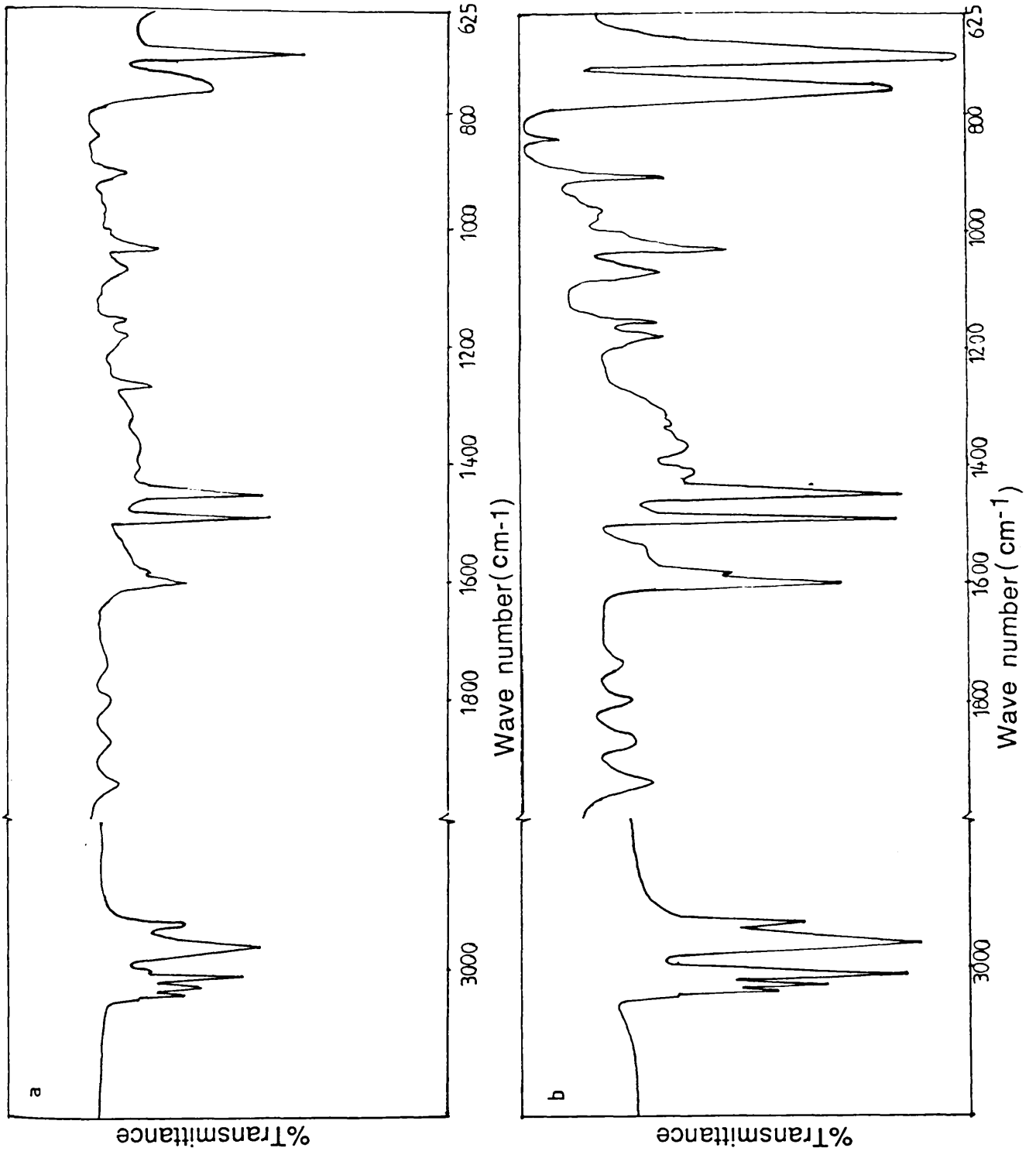


Fig. 7.15. Infrared spectra of the involatile residue from degradation of metal salts of dicarboxyl-terminated Polystyrene, isothermaly heated at 350 ^{o}C for 20 min under TVA conditions. (a) Ca, (b) Zn.

2.2.2.3b. Cold ring fraction

The IR spectra of cold ring fractions were indicated the presence of vinyl and carbonyl groups with short chain fragments.

2.2.2.3c. Residue

The main constituents of the involatile materials in all three polymer samples the were respective metal carbonates and metal oxides. It was also observed that sodium and calcium oxides were very reactive and reacted with atmospheric carbon dioxide to give sodium and calcium carbonates.

2.2.2.4. Product Analysis

In this investigation, minor products have been examined by GC-MS for sodium, calcium and zinc metal salts of dicarboxyl-terminated polystyrene samples degraded isothermally at 300 ^{o}, 350^{o}, and 420 ^{o}C for 20 min in each case under TVA conditions. The GC-MS chromatograms for products of degradation of 100 mg in each polymer sample at 350 ^{o}C for 20 min are shown in Figs. 7.16, 7.17 and 7.18. The GC-MS results indicate the formation of benzene is in significant amount from Zn salt but there is no significant amount of benzene from Na and Ca salts.

The same polymer samples were heated for a further 20 min at 420 ^{o}C. The GC-MS data indicate styrene was as principal product together with toluene and α-methylstyrene next in importance in all three polymer samples at these temperatures (300^{o}, 350^{o} and 420 ^{o}C). There are some other minor products, observed at each degradation temperature which are listed in Table 7.10.

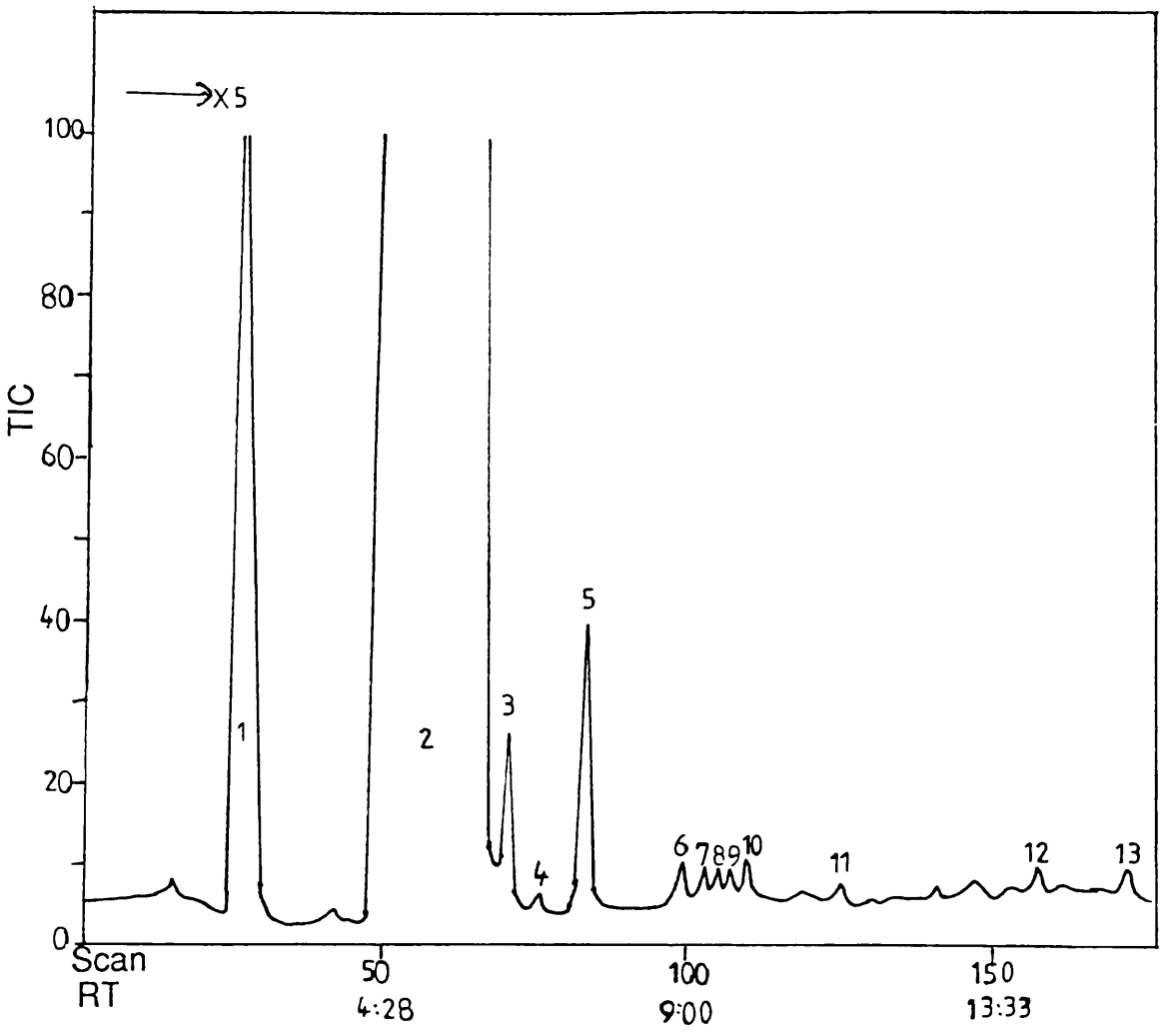


Fig. 7.16. GC data for the volatile liquid fraction of sodium salt of dicarboxyl-terminated Polystyrene, degraded isothermally at 350 ^{o}C for 20 min,under TVA conditions.

Assignments:1; Toluene, 2; Styrene, 3; Allylbenzene, 4; Benzaldehyde, 5; α-methylstyrene, 6; Methylindene, 7; Cyclopropylbenzene, 8; 4-phenyl-1-butene, 9; Nor-butylbenzene, 10; Methylindane, 11; Acetophenone, 12; Naphthalene, 13; Unknown.

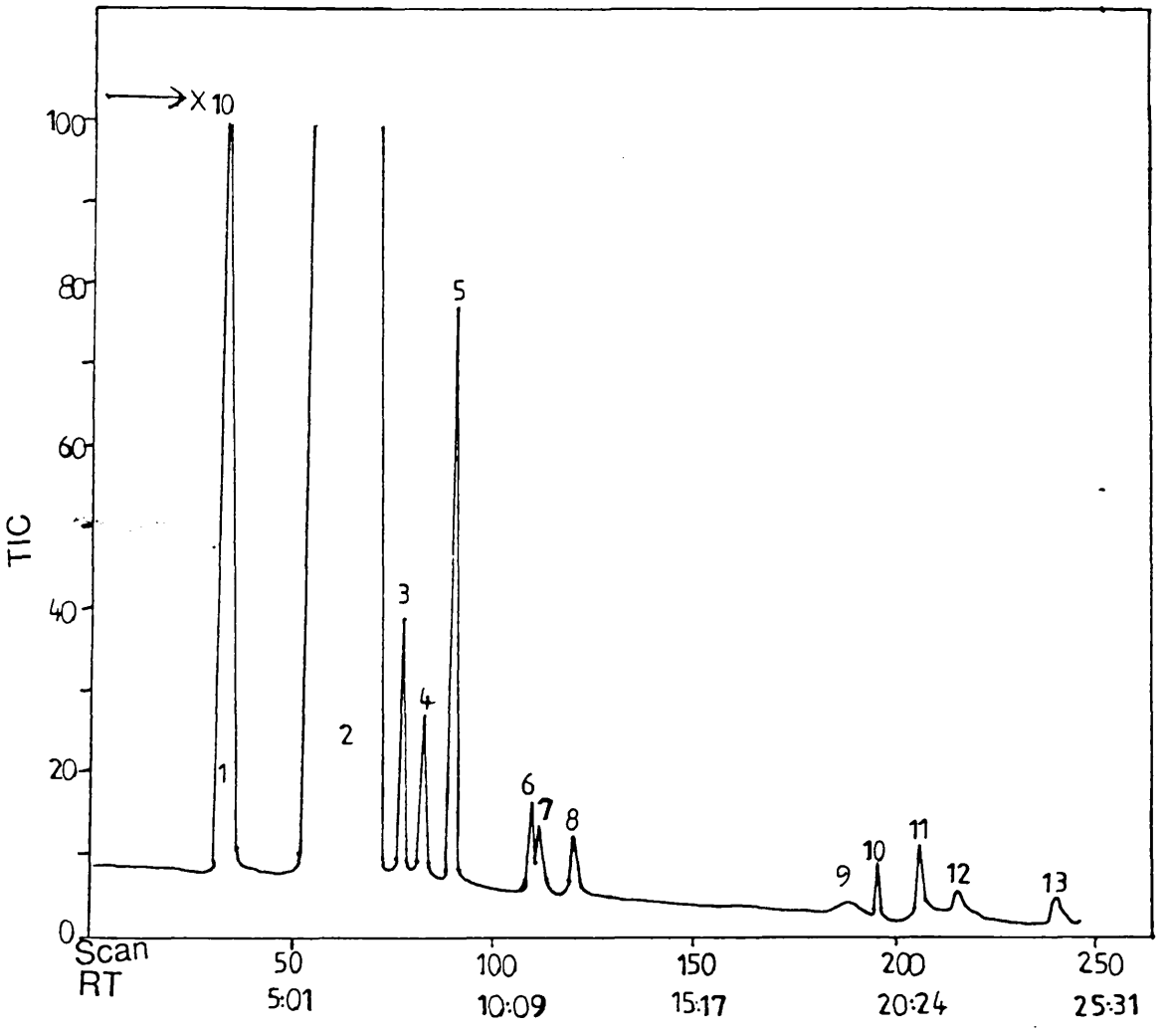


Fig. 7.17. GC data for the volatile liquid fraction of calcium salt of dicarboxyl-terminated Polystyrene, degraded isothermally at 350 ^{o}C for 20 min, under TVA conditions.

Assignments:1; Toluene, 2; Styrene, 3; Allylbenzene, 4; Benzaldehyde, 5; α-methylstyrene, 6; Cyclopropylbenzene, 7; Methylindene, 8; 4-phenyl-1-butene, 9; Unknown, 10; Unknown, 11; Naphthalene, 12; 2-phenylethyl alcohol, 13; Phenylacetaldehyde.

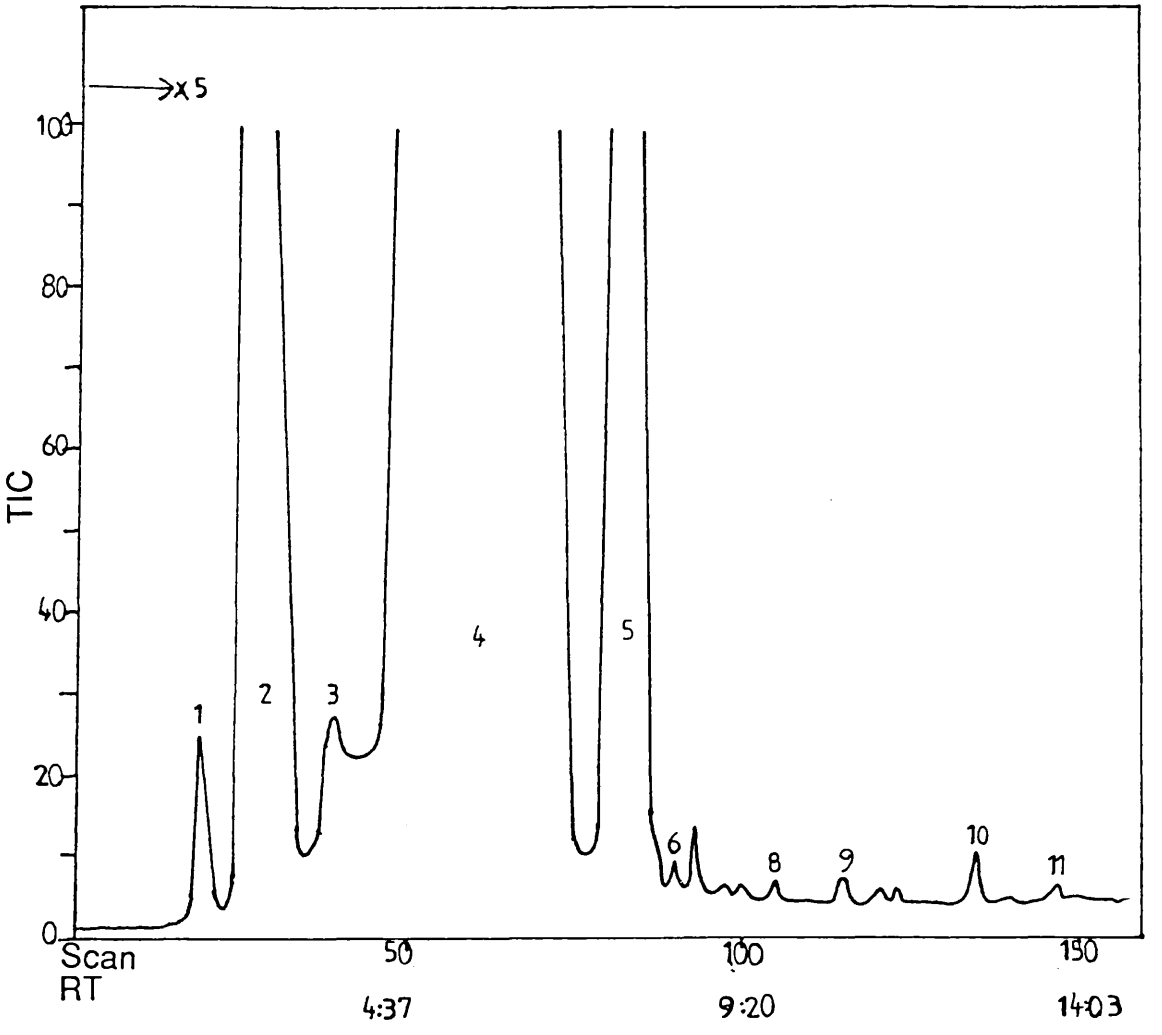


Fig. 7.18.GC data for the volatile liquid fraction of zinc salt of dicarboxyl-terminated Polystyrene, degraded isothermally at 350 ^{o}C for 20 min, under TVA conditions.

Assignments:1; Benzene, 2; Toluene, 3; Ethylbenzene, 4; Styrene, 5; α-methylstyrene, 6; Cyclopropylbenzene, 7; Unknown, 8; Methylindane, 9; Acetophenone, 10; Naphthalene, 11; Unknown.

Table 7.10 GC-MS Results for Condensable Volatile Products Evolved from Dicarboxyl-Terminated Polystyrene Containing Na, Ca and Zn Metals , Heated Isothermally at 300°, 350° and 420 °C for 20 min in Each Step Under TVA Conditions.

	NaO_2C-PS-CO_2Na	~O_2C-PS-CO_2Ca~	~O_2C-PS-CO_2Zn~
Common products evolved for all polymers at all temperatures	Styrene, Toluene, α-methylstyrene		
300 °C	Allylbenzene Acetophenone Naphthalene	Allylbenzene 4-phenyl-1-butene Phenylacet-aldehyde Cyclopropyl benzene	Ethylbenzene Benzaldehyde Acetophenone
350 °C	Allylbenzene Benzaldehyde Methylindene Methylindane Butylbenzene Cyclopropyl benzene	2-phenyl ethyl alcohol Indane	Ethylbenzene Benzene Cyclopropyl benzene Phenyl propionaldehyde Methylindane Indane
420 °C	Allylbenzene Cyclopropyl benzene Indene Ethylbenzene	Allylbenzene Ethylbenzene Indene	Ethylbenzene Benzene Methylindene Cyclopropyl benzene

3. MECHANISM OF DEGRADATION

The thermal degradation behaviour of polystyrene and dicarboxyl-terminated polystyrene has already been discussed in Chapters Five and Six, respectively.

The thermal degradation of styrene-acrylic acid copolymers and their sodium and zinc salts has been studied by different workers.[101-103] Similarly the thermal degradation of styrene-methacrylic acid copolymers has also been studied.[104] Nothing has been published however, about the mechanism of thermal degradation of Na, Ca and Zn salts of dicarboxyl-terminated polystyrene. In the present studies, it has been seen that the main mechanism of thermal degradation is the same as for normal polystyrene as described in Chapter Five.

At temperatures below 300 ^{o}C, chain scission occurs and generates radicals A and B. These radicals undergo disproportionation, to produce benzylic and vinylidene chain ends. At higher temperatures, further homolysis occurs and the vinylidene chain ends give α-methylstyrene and radical A, which depropagates to monomer. Similarly, homolysis at benzylic ends produces toluene.

In this investigation some minor products such as methylindane, 4-phenyl-1-butene, ethylbenzene and methylindene were also identified. It has been assumed that the mechanism of formation of these products is the same as described for normal polystyrene.

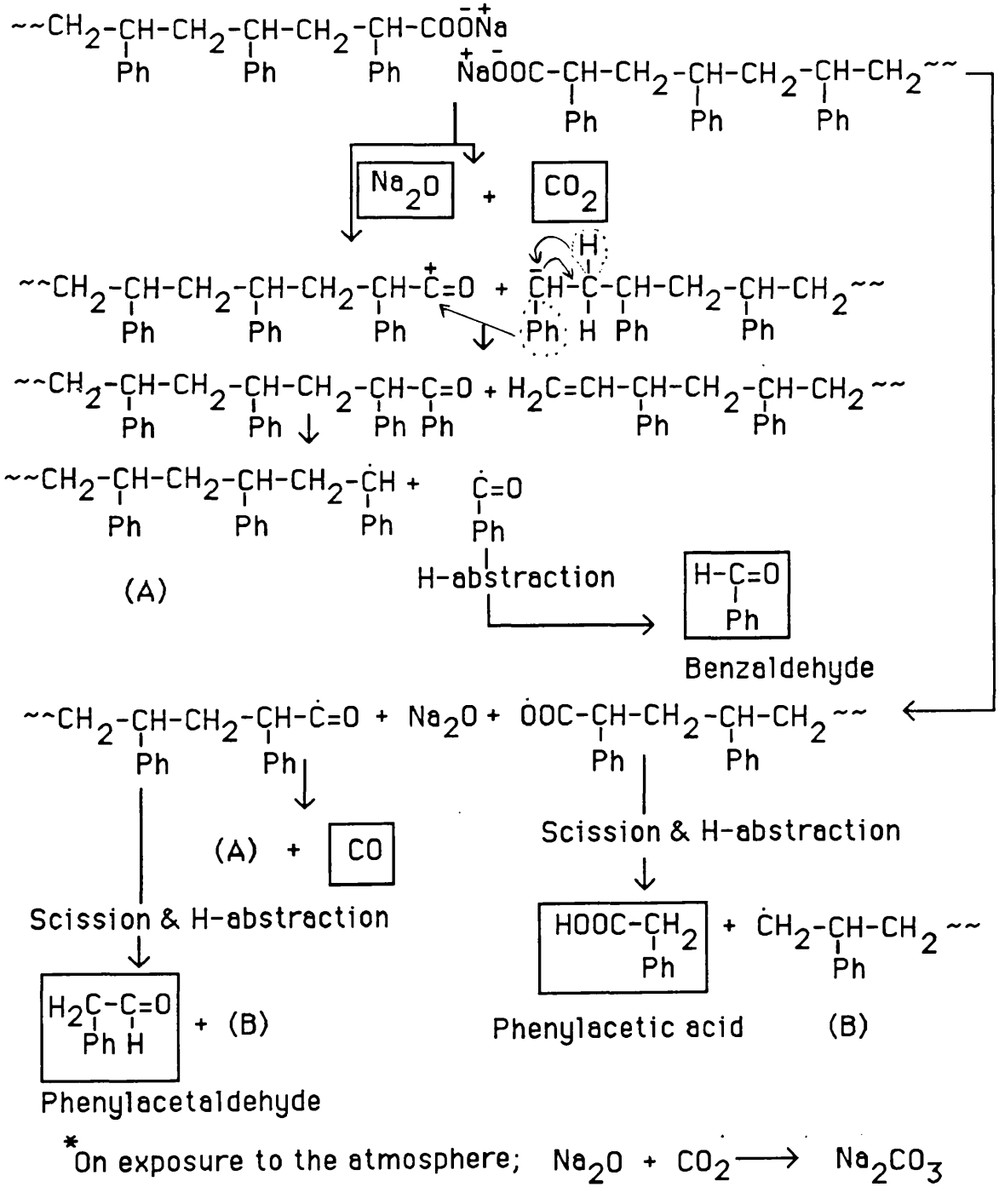
Some other minor products, however, have also been identified which are associated with the presence of metal carboxylate in the polymer chain. The mechanisms of formation of these products are shown in schemes 1, 2 and 3, respectively. The formation of these products has been found to occur mainly at the onset of volatilisation.

4. CONCLUSIONS

According to the TG, DTG, DTA and TVA data which have been discussed , the sodium, calcium and zinc salts of dicarboxyl-terminated polystyrene are slightly more stable than dicarboxyl-terminated polystyrene. Although the differences in the salt polymers are very small, the Zn salt polymer is less stable in comparison with Na and Ca salt polymers.

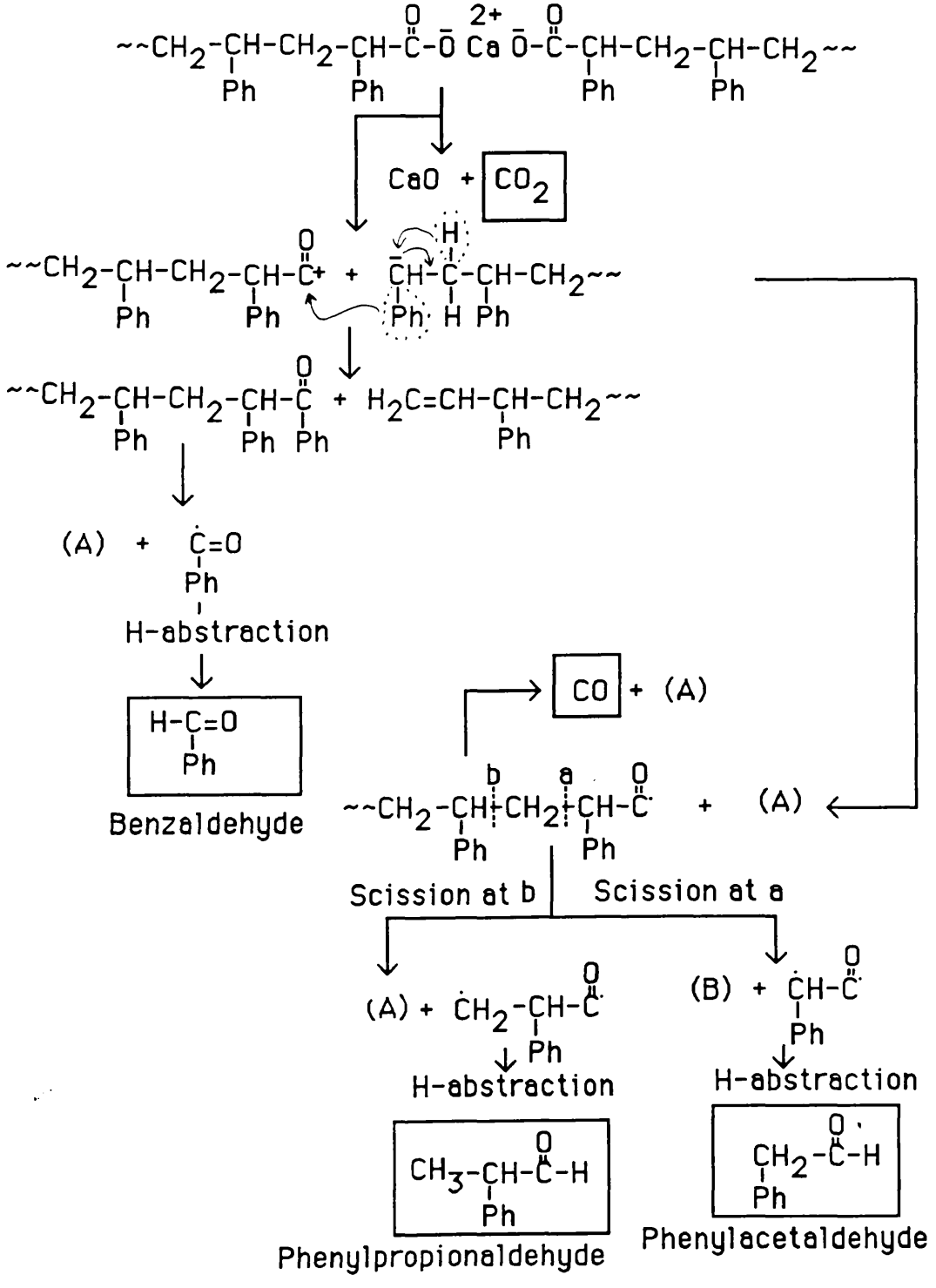
The nature of the volatile gaseous products and the volatile liquid products evolved during degradation of these polymers suggest a similar mechanism of degradation but the cold ring fraction products from the zinc salt of dicarboxyl-terminated polystyrene showed differences from those polymers with sodium and calcium salt linkages.

Scheme 1 Mechanism of Formation of Minor Products from Chain Ends in Degradation of $NaO_2C\text{-}PS\text{-}CO_2Na$

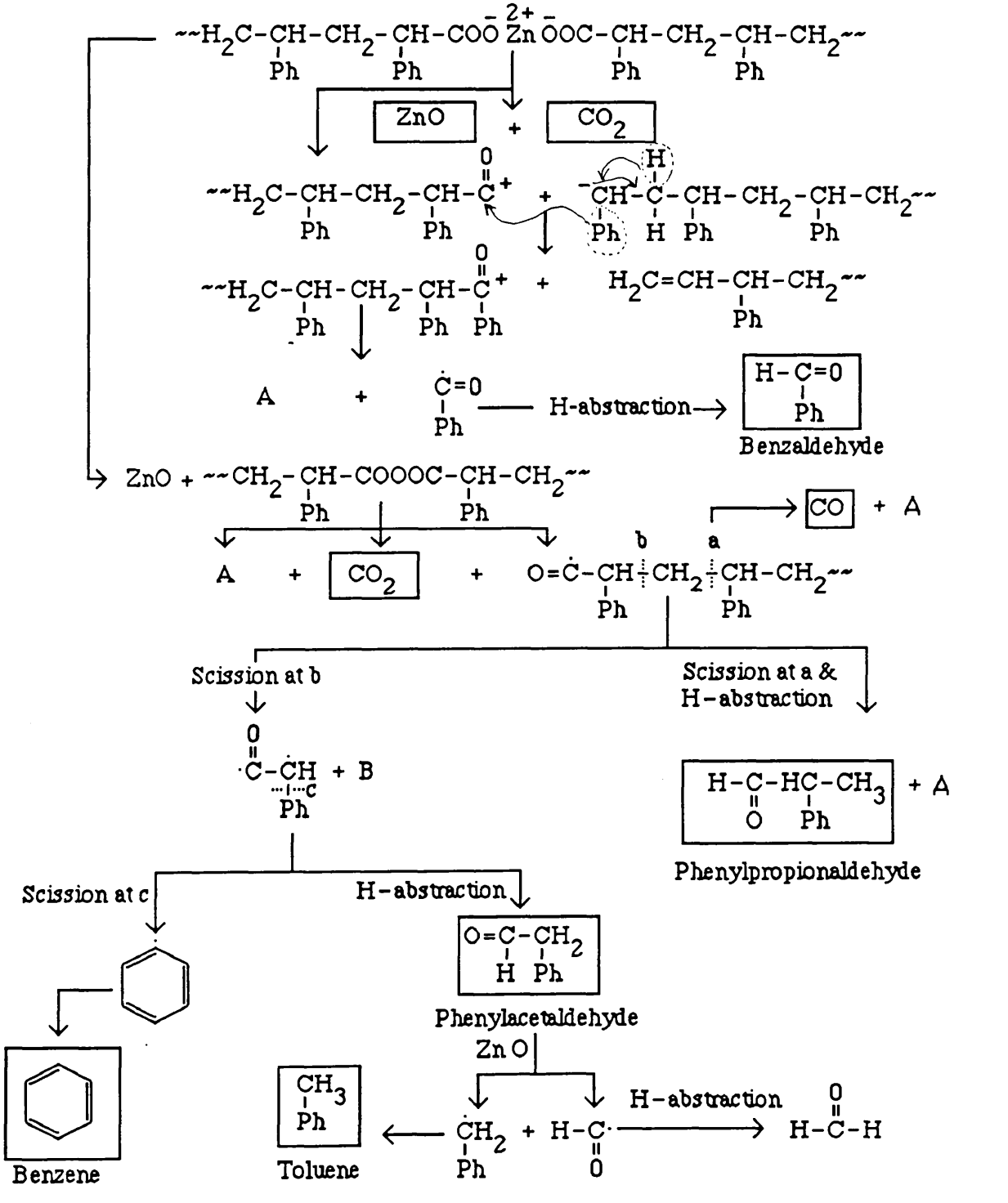


*On exposure to the atmosphere; $Na_2O + CO_2 \longrightarrow Na_2CO_3$

Scheme 2 Mechanism of Formation of Minor Products from Chain Ends in Degradation of ~~O_2C-PS-CO_2-Ca~~



Scheme 3 Mechanism of Formation of Minor Products from Chain Ends in Degradation of ~~O_2C-PS-CO_2-Zn~~



CHAPTER EIGHT

THERMAL BEHAVIOUR OF LINKED BLOCK POLYSTYRENE

1. INTRODUCTION

Block copolymerisation is commonly used in industry to obtain a desired set of physical properties in a polymeric material. It has been shown that living polymer can initiate the anionic polymerisation of another monomer.[161,163] When the second monomer is added after full consumption of the first, a block copolymer results. The procedure can be repeated and a polymer with several blocks can be prepared. The addition of a second monomer to a living polymer with two active ends leads to a triblock copolymer.

The thermal behaviour of block copolymers is of interest since a block copolymer may have degradation properties considerably different from those of the corresponding homopolymers. The presence of a block of monomer may either stabilise or destabilise the block copolymer relative to the homopolymers. It is therefore important to understand how such materials breakdown on heating.

In the present studies, linked block polystyrene samples were prepared. They are materials with blocks of polystyrene chain joined by groups which might be expected to modify the properties of normal polystyrene.

These modified polystyrene samples were achieved by a coupling reaction of diacid chloride-terminated polystyrene with 1,6-diaminohexane and 2,2̄-dihydroxy-4,4̄-dimethoxybenzophenone, not by addition copolymerisation, as in

block copolymers.

The thermal behaviour of these linked block polystyrene samples was studied and their mechanisms of degradation were elucidated. The degradation behaviour of these modified polystyrene has not been studied previously.

The introduction of these linking of units (1,6-diaminohexane and 2,2́-dihydroxy-4,4́-dimethoxybenzophenone) into the backbone in this way might be developed to achieved specific changes to the properties of polystyrene (e.g. improved thermal or photostability, fire retardance, photo-instability or biodegradability).

1.2. POLYMER PREPARATION

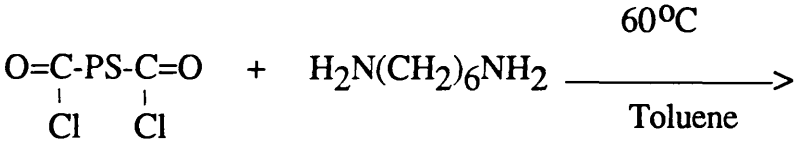
The coupling reactions through which these modified polystyrene samples are formed are based on reactions between polystyrene with terminal carboxylic acid derivatives and small bifunctional amino or hydroxyl compounds which lead to the formation of amides, esters etc. Essentially, these reactions convert one derivative of carboxylic acid into another.

The acid chlorides are the most reactive derivatives of carboxylic acid and were therefore selected for use in these coupling reactions.

1.2.1. PREPARATION OF DIACID CHLORIDE-TERMINATED POLYSTYRENE

Diacid chloride-terminated polystyrene was prepared by reacting dicarboxyl-terminated polystyrene with thionyl chloride as described in Chapter Three.

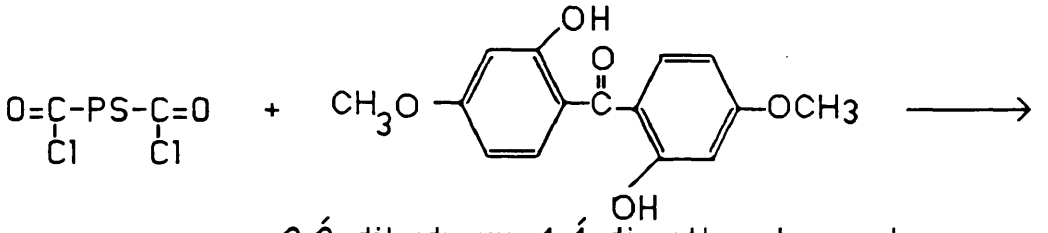
1.2.2. Preparation of Amide Linked Block Polystyrene[59-63]



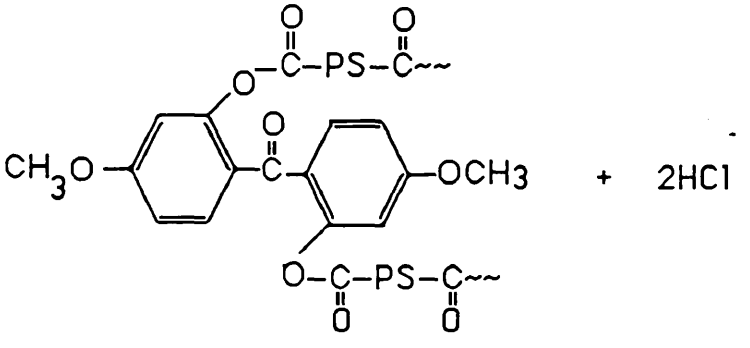
$$\sim\sim OC\text{-}PS\text{-}CO\text{-}NH\text{-}(CH_2)_6\text{-}NH\sim\sim + 2HCl$$

A dilute (5%) toluene solution of diacid chloride-terminated polystyrene was poured into a round bottomed flask. Then 60 equivalents of 1,6-diaminohexane were added. The reaction solution was refluxed at 60 °C for 12 hours. The aminated polystyrene was precipitated in acidified methanol, redissolved in THF and reprecipitated in AR grade methanol. The polymer was dried under vacuum and stored in a desiccator.

1.2.3. Preparation of Ester Linked Block Polystyrene[162]



2,2́-dihydroxy-4,4́-dimethoxybenzophenone



A 50 ml three necked flask equipped with mechanical stirrer and nitrogen inlet and an exit for hydrogen chloride was assembled. 3g of diacid chloride-terminated polystyrene and 1g of 2,2́-dihydroxy-4,4́-dimethoxybenzophenone were placed in the flask and heated until melting occurred. The mixture was stirred vigorously and nitrogen was passed through the reaction to avoid accumulation of hydrogen chloride. The temperature was raised to 160 ^{o}C and held at that temperature for one hour. The polymer was obtained as a yellow solid It was dissolved in THF and reprecipitated in Analar methanol. The polymer was dried under vacuum and stored in a desiccator.

1.3. CHARACTERISATION OF LINKED BLOCK POLYSTYRENE

Diacid chloride-terminated polystyrene and its reaction products with 1,6-diaminohexane and 2,2́-dihydroxyl-4,4́-dimethoxybenzophenone, respectively, were characterised by elemental analysis, gel permeation

chromatography (GPC) and infrared spectroscopy.

1.3.1. Elemental Analysis

The percentages of carbon, hydrogen, nitrogen and halogen (chlorine) were obtained from microanalysis. The percentage of oxygen was calculated by difference. The microanalysis data are given in Table 8.1.

1.3.2. Gel Permeation Chromatography

The molecular weights of these three polymer samples were obtained as a service from Polymer & Supply Characterisation Centre, using THF as solvent. Molecular weight data are given in Table 8.2.

1.3.3. Infrared Spectroscopy

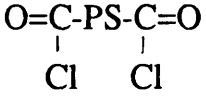
The IR spectrum of diacid chloride-terminated polystyrene has been given on page 63. The IR spectra of the linked block polystyrenes ~OC-PS-$CONH(CH_2)_6NH$~ and ~OC-PS-COR~ were obtained by the KBr disc technique using 1-2 mg of sample and 300 mg of KBr. IR spectra of amide and ester linked block polystyrene samples are given in Fig. 8.1(a,b). The characteristic bands due to O-C=O, N-C=O, H-N, C=C and C-H stretching are clearly shown in the spectra and the assignment of the peaks is summarised in Table 8.3.

2. THERMAL DEGRADATION OF LINKED BLOCK POLYSTYRENE

There are no previous reports of studies of polymers of these types. It might be expected that at elevated temperature carbon-nitrogen and carbon-oxygen in the backbone may break and additional volatile products may be produced but the main decomposition would be expected to be the same as in normal polystyrene ,

Table 8.1 Analytical Data

Polymer	Calculated					Observed				
	%C	%H	%O	%N	%Cl	%C	%H	%O	%N	%Cl
A	88.61	7.34	1.28	Nil	2.8	88.89	7.25	1.28	Nil	2.58
B	90.19	7.35	1.30	1.43	Nil	90.12	8.24	0.17	1.47	Nil
C	88.50	7.27	4.15	Nil	Nil	87.84	7.91	4.25	Nil	Nil

A = 

B = ~~OC-PS-CONH$(CH_2)_6$-NH~~

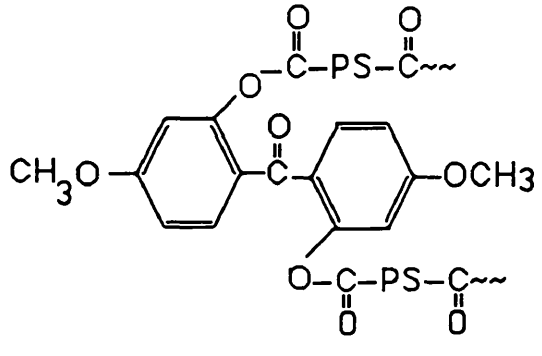
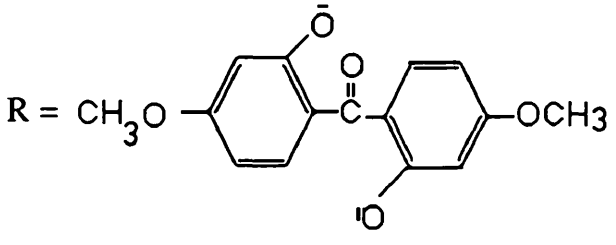
C = 

Table 8.2 Molecular Weight Data for Diacid Chloride-Terminated Polystyrene and Linked Block Polystyrene Samples.

Polymer	Mn by GPC	Mw/Mn
ClOC-PS-COCl	2,500	1.32
~~OC-PS-CONH-$(CH_2)_6$-NH~~	206,400	1.59
~~OC-PS-CO-R~~	6,454	1.64



described previously. In this study, TVA, TG and DTA techniques were used. The condensable volatile products at -196 ^{o}C obtained by degradation under TVA conditions were separated by the SATVA method.

2.1. PROGRAMMED HEATING EXPERIMENTS

2.1.1. Thermal Volatilisation Analysis

Powder samples of 80 mg were used. All degradations were performed using programmed heating at 10 ^{o}C/min to 500 ^{o}C under normal TVA conditions as described in Chapter Two.

TVA curves obtained for ~~OC-PS-CONH$(CH_2)_6$NH~~ and ~~OC-PS-COR~~ linked block polystyrene samples are reproduced in Fig. 8.2(a,b). No volatile products are given off at temperatures below 300 ^{o}C. Above this temperature the release of volatile materials commences including very small amounts of non-condensable products. The -45 ^{o}C trace is well separated from 0 ^{o}C, but after T_{max}, it begins to cross the 0 ^{o}C trace, indicating a limiting rate effect due to formation of styrene. Fig. 8.2(b) shows more separation between traces (-75^{o}, -100^{o}, -196 ^{o}C) in comparison with that of Fig. 8.2(a).

It should be observed, however, that the T_{max} temperature of the peak for the both linked block polystyrene samples lies above that of the dicarboxyl-terminated polystyrene sample.

The thermal stability of these linked block polystyrene seems to be similar to that of normal polystyrene. Gravimetric data were obtained under TVA conditions to 500 ^{o}C, in which a linked block polystyrene sample was placed in a thin glass sample bottle and weighed after the experiment. The gravimetric data are given in Table 8.4.

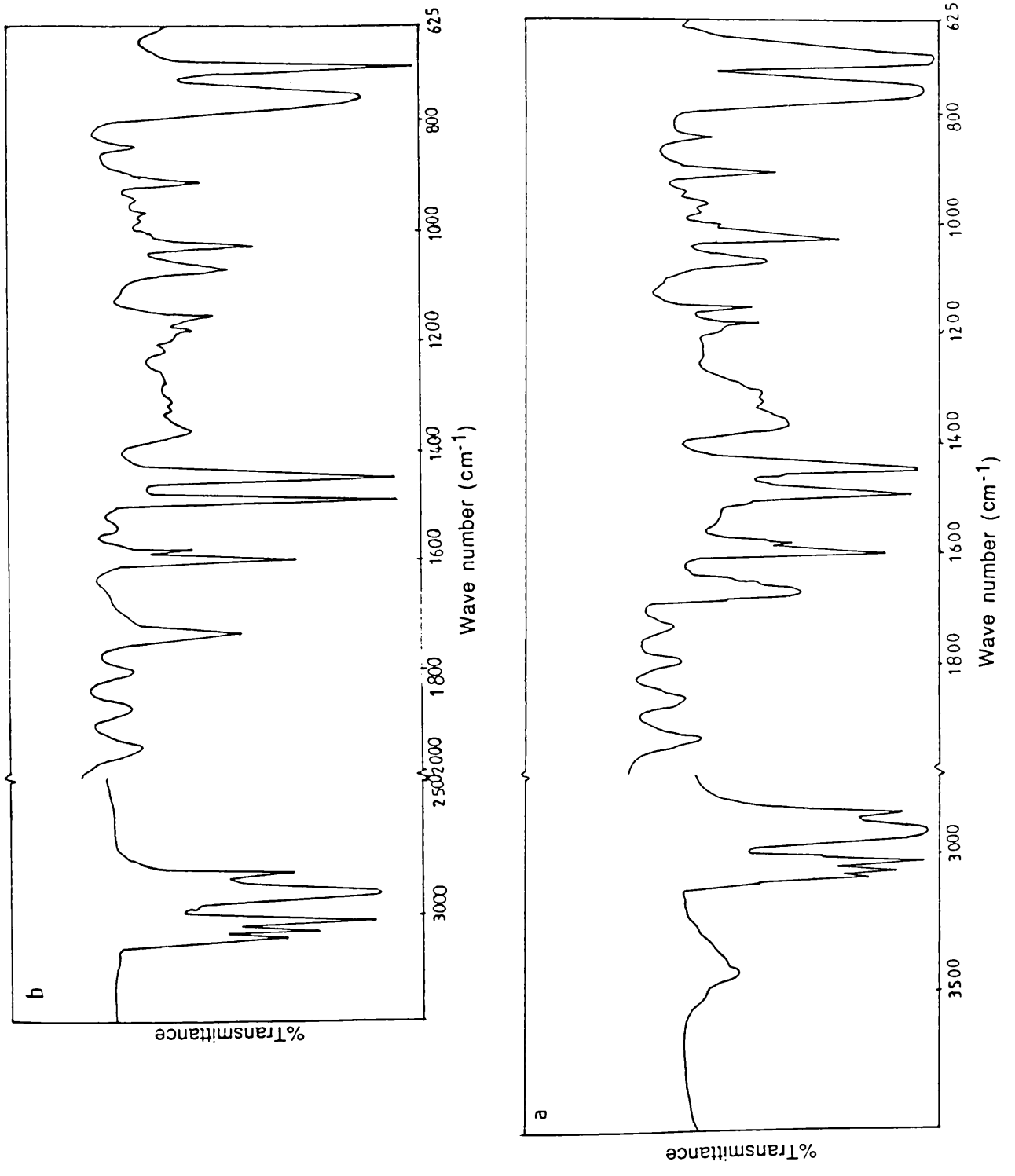


Fig. 8.1a. FTIR spectrum of the amide linked block Polystyrene.

Fig. 8.1b. FTIR spectrum of the ester linked block Polystyrene.

Table 8.3 Assignment of IR Peaks of Linked Block Polystyrene Samples.

Polymer	Frequencey (cm^{-1})	Mode	Group
	3460-3400 (m)	N-H stretching	secondary amide
	3090 (m)	C-H stretching (asymmetrical)	
	3043 (s)	C-H stretching (symmetrical)	aryl-H
	2910-2850 (m)	C-H stretching	saturated C-H
B	2000-1800 (w)	overtone	monosubstituted aromatic ring
	1650-1580 (s)	C=O stretching	amide group
	1600-1580 (m)		aromatic ring system
	1468 (s)	C-H bending	C-H
	1055 (m)	CH_2 rock	
	952 (s)	CH_2 wag	
	780-720 (s)	C-H out of plane deformation	monosubstitiuted aromatic ring
	3080-3040 (m)	C-H stretching	aryl-H
	2910-2850 (m)	C-H stretching	saturated C-H
	2000-1800 (w)	overtone	monosubstituted
C			aromatic ring
	1740 (s)	C=O stretching	aryl ester
	1600-1580 (m)		aromatic ring system
	1305 (s)	C-O stretching	ester
	1050 (m)	CH_2 rock	
	780-680 (s)	C-H out of plane deformation	monosubstituted aromatic ring

m=medium, s=sharp (strong), w=weak

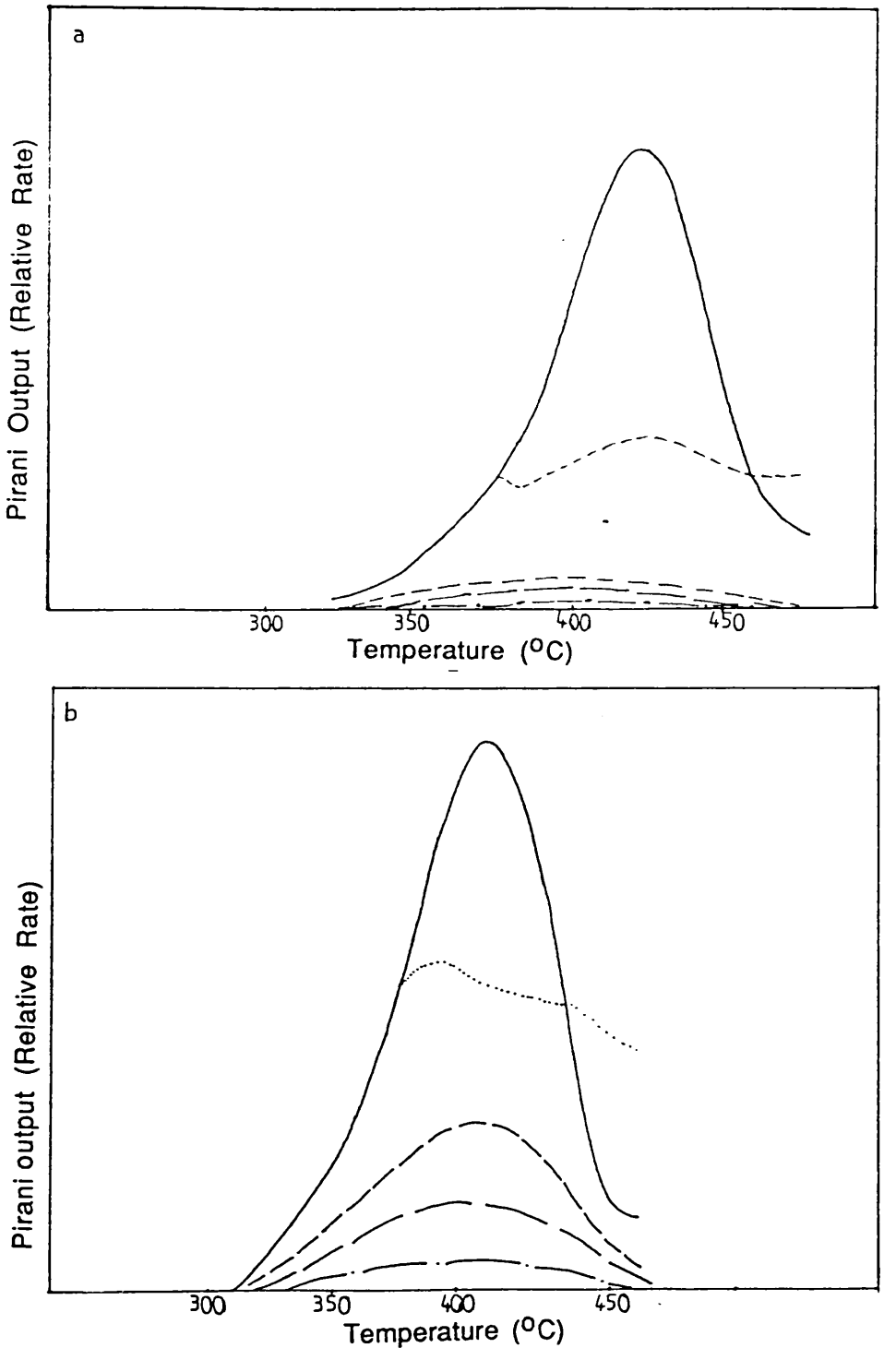


Fig. 8.2. TVA curves for linked blocked Polystyrenes.

(a) Amide and (b) Ester linked block Polystyrene.

Keys: ___ 0^{o}, ...-45^{o}, - - - =75^{o}, __ __ -100^{o}, __ . __ -196 ^{o}C.

2.1.2. Subambient Thermal Volatilisation Analysis

Condensable volatile products from degradation of linked block polystyrene samples were fractionated by the SATVA technique. SATVA traces in the case of ~~OC-PS-CONH$(CH_2)_6$NH~~ and ~~OC-PS-COR~~ are shown in Figs. 8.3 and 8.4, respectively. Products were collected in three different fractions in each linked block polystyrene sample. The first two fractions were collected as condensable gaseous products and third (last) fraction was collected as a condensable liquid products.

2.1.3. Product Analysis

The degradation products have been examined by infrared spectroscopy, mass spectrometry, ^1H nuclear magnetic resonance spectrometry and GC-MS techniques.

2.1.3.1. Residue

No residue was obtained in the degradation of the ~~OC-PS-COR~~ sample, but a 4% residue was obtained in the degradation of the ~~OC-PS-CONH$(CH_2)_6$NH~~ sample under normal TVA conditions to 500 ^oC. The IR spectrum of the residue is reproduced in Fig. 8.5. The poorly resolved spectrum shows two broad bands between 1650-1400 cm^{-1} and 1150-1050 cm^{-1}. It also shows small bands at 890 cm^{-1} and 700 cm^{-1}. These absorption frequencies could be due to the presence of an ammonium salt.

2.1.3.2. Cold Ring Fraction

Cold ring fractions were examined by IR, NMR and MS. The corresponding IR spectra (Fig. 8.6 a,b) are rather similar to the spectra of the linked block

Table 8.4 TVA Data from Degradation of ~~OC-PS-CONH$(CH_2)_6$NH~~ and ~~OC-PS-CO-R~~ Samples Under TVA Conditions to 500 °C.

Polymer	Initial decomp-osition temp., °C	T_{max} °C	Wt% residue at ~500 °C	Wt% CRF at ~ 500 °C	Wt% conden-sable volatile products at ~ 500 °C
~OC-PS-CONH$(CH_2)_6$NH~	325	423	4.0	40.0	45.0
~~OC-PS-CO-R~~	310	410	Nil	40.5	43.5
PS37	312	412	Nil	31.2	68.2

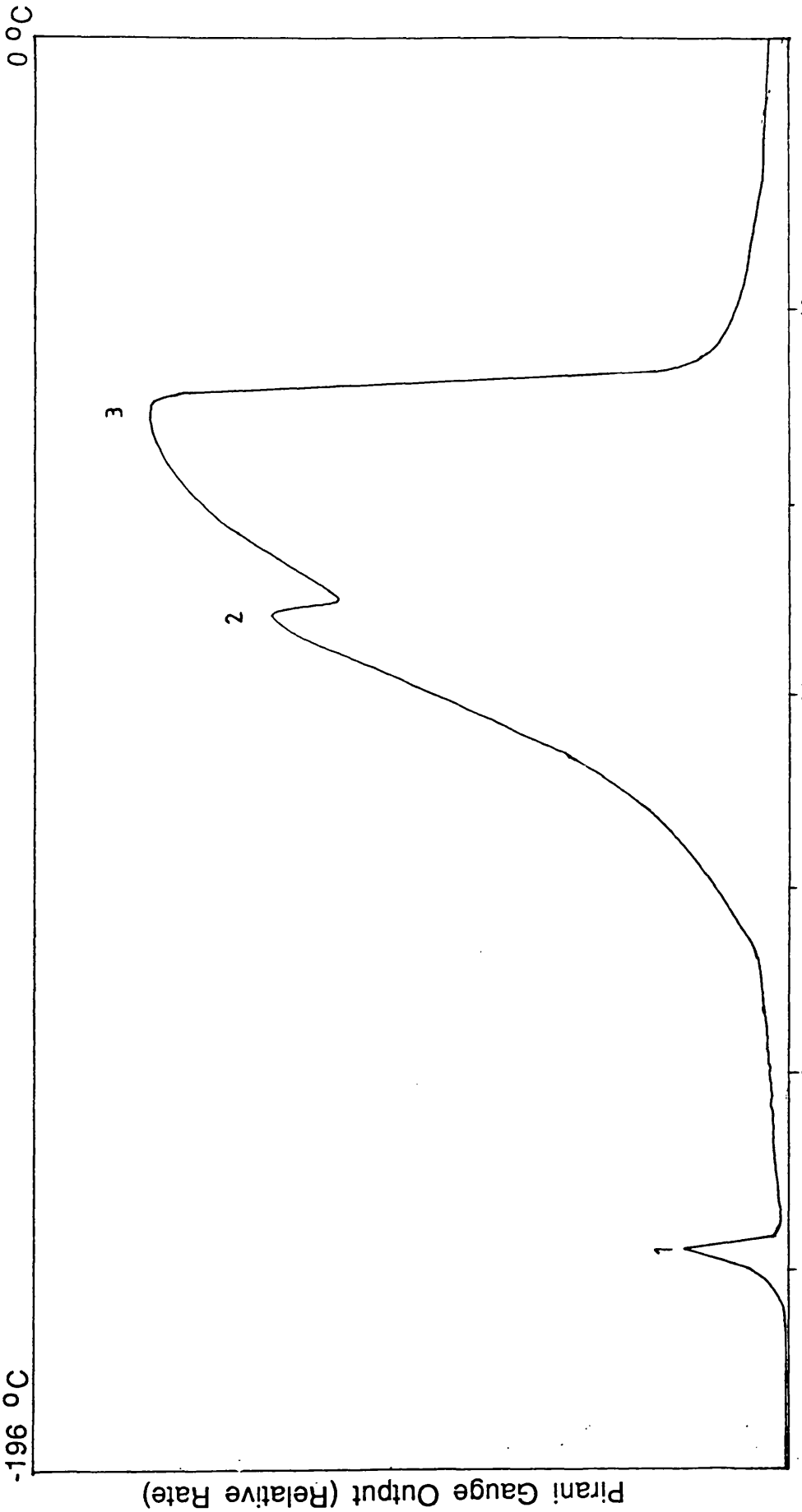


Fig. 8.3. SATVA curve of the condensable product fraction from degradation to 500 °C under TVA conditions of amide linked block Polystyrene.

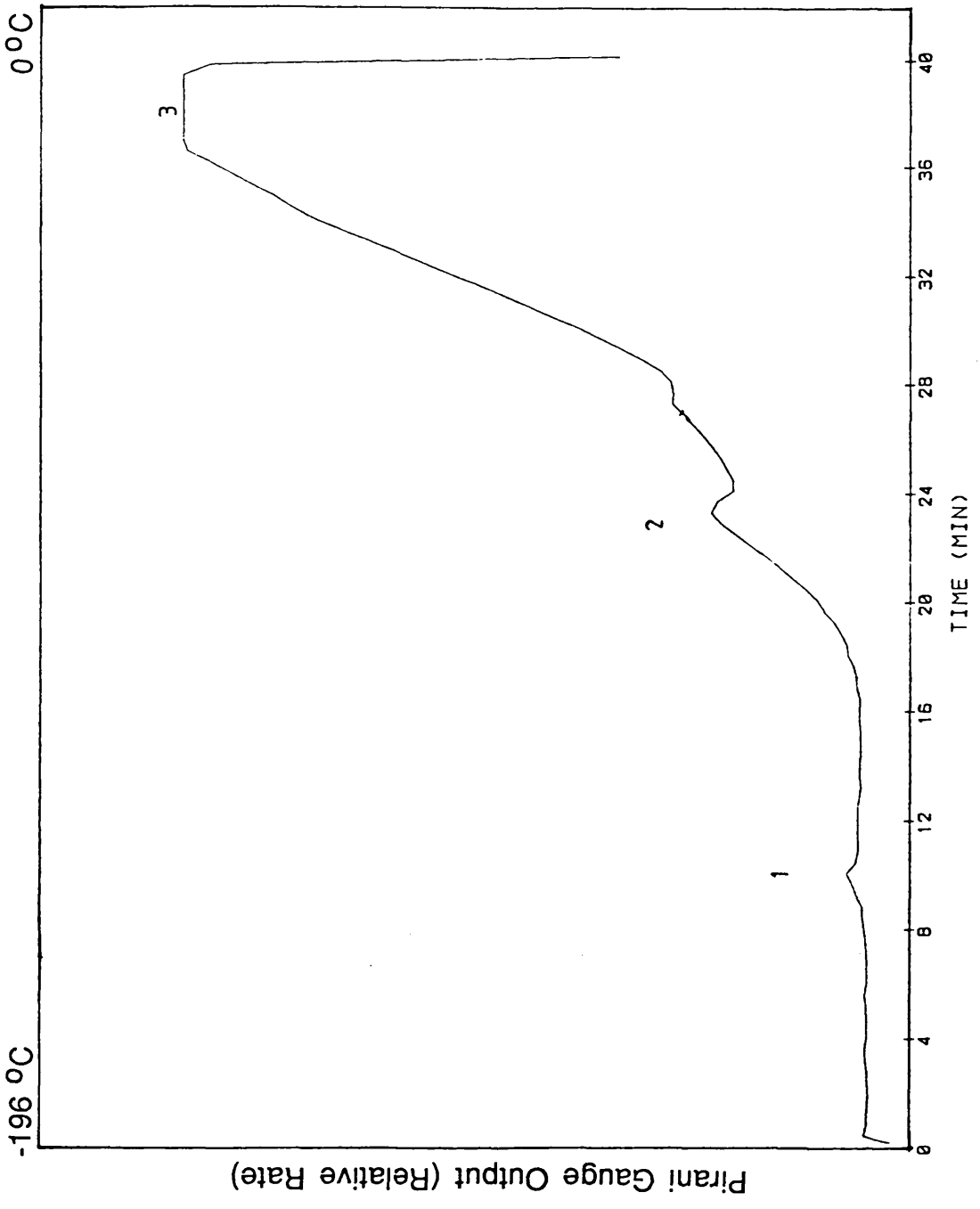


Fig. 8.4. SATVA curve of the condensable product fraction from degradation to 500 °C under TVA conditions of ester linked block Polystyrene.

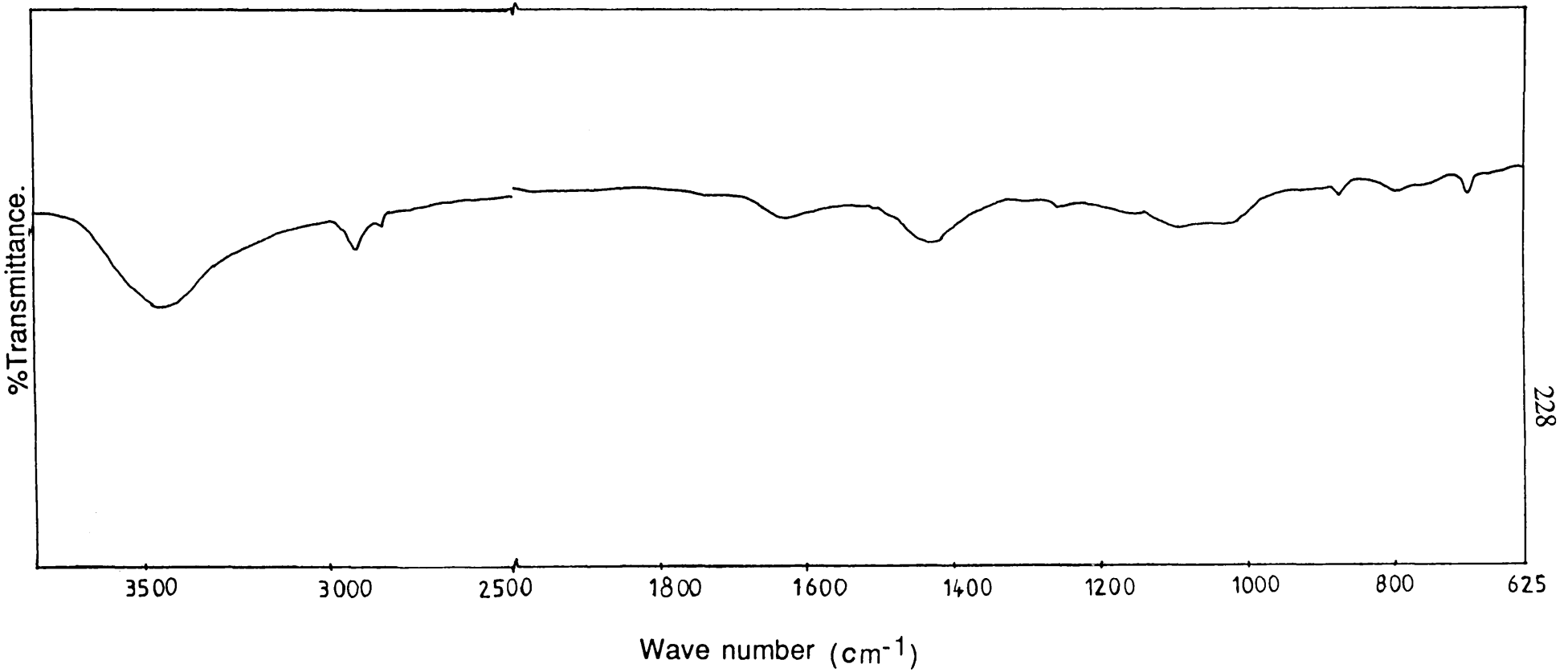


Fig. 8.5. Infrared spectrum of residue from degradation to 500 ^{o}C of amide linked block Polystyrene.

polymers, showing bands at 1680 and 1710, 1740 cm^{-1} due to amide, carbonyl and carboxyl group absorptions, respectively. The characteristic bands of primary and secondary amide group were at 3410, 3300 cm^{-1}. The assignment of the peaks is summarised in Table 8.5. Products identified from the CRF of linked block polystyrene samples are listed in Table 8.6 and 8.7.

2.1.3.3. Condensables as Gaseous Products

The condensable gaseous products were examined by IR spectroscopy and mass spectrometry. IR spectra of gaseous volatile products from the degradation of ~~OC-PS-CONH$(CH_2)_6$NH~~ are shown in Fig. 8.7. These products clearly consist of carbon dioxide, ammonia and a trace of isocyanic acid. The second fraction from the SATVA separation was collected in a gas cell. The IR spectrum and mass spectrometry data indicated that it consists of toluene and benzene.

The condensable gaseous products of degradation of ~~OC-PS-CO-R~~ were collected in two fractions. The IR spectra indicated carbon dioxide and toluene, respectively. The second fraction was also subjected to MS analysis which indicated the presence of methanol in addition to toluene.

2.1.3.4. Non-Condensable Gases

Carbon monoxide was established as the non-condensable material present.

2.1.3.5. Condensables as Liquid Fraction

The IR spectra in Fig. 8.8(a,b) indicate that this fraction in both cases consists of styrene. There are additional absorption at 1700 cm^{-1} and 1690 cm^{-1}.

Mass spectrometric analysis confirmed styrene as a principal product, as in

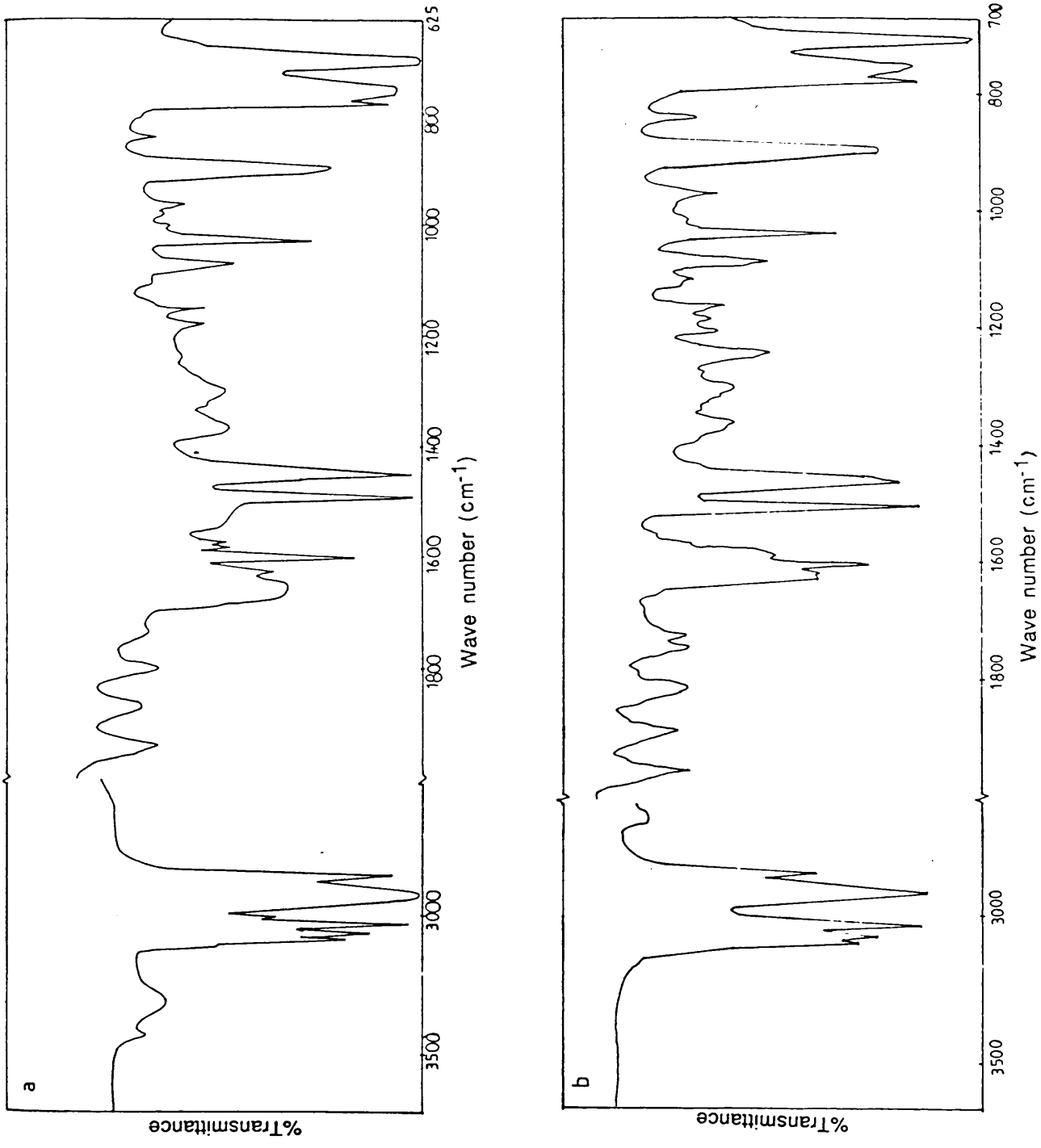


Fig. 8.6. Infrared spectra of cold ring fraction from degradation of linked block Polystyrenes to 500 ^{o}C. (a) Amide (b) Ester.

Table 8.5 Assignment of IR Peaks of Cold Ring Fractions from degradation of ~~OC-PS-CONH-$(CH_2)_6$-NH~~ and ~~OC-PS-CO-R~~ to 500 ^oC under TVA Conditions.

CRF of	Frequencey (cm-1)	Remarks
B	3460-3400 (w)	secondary amide N-H stretching
	3410-300 (b)	typical amide -NH_2 pair of bands: the unsymmetrical and symmetrical stretching
	3085-3010 (s)	aryl-H stretching
	2930-2840 (m)	saturated C-H stretching
	2000-1800 (w)	monosubstituted aromatic ring pattern
	1680-1650 (m)	primary amide
	1650-1580 (w)	secondary amide
	1620-1630 (m)	C=C vinyl stretching
	1600-1580 (m)	aromatic ring
	980-910 (s)	C-H deformation in vinyl group
	770-680 (s)	monosubstitution pattern of the aromatic ring
C	3040-3010 (s)	aryl-H stretching
	2930-2840 (m)	saturated C-H stretching
	2000-1800 (w)	monosubstituted aromatic ring pattern

1740 (s)	C=O stretching in ester
1710 (m)	C=O stretching of carbonyl group
1630-1620 (m)	C=C stretching with conjugation
1600-1580 (m)	aromatic ring vibrations
1250-1210 (m)	C-O stretching in ester
980-910 (m)	C-H deformation in vinyl group
780-720 (m)	C-H bending vibration
720-680 (s)	monosubstitution pattern of aromatic ring

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s=sharp (strong), b=broad, m=medium, w=weak

B = ~~CO-PS-CONH-$(CH_2)_6$-NH~~

C= ~~CO-PS-CO-R~~

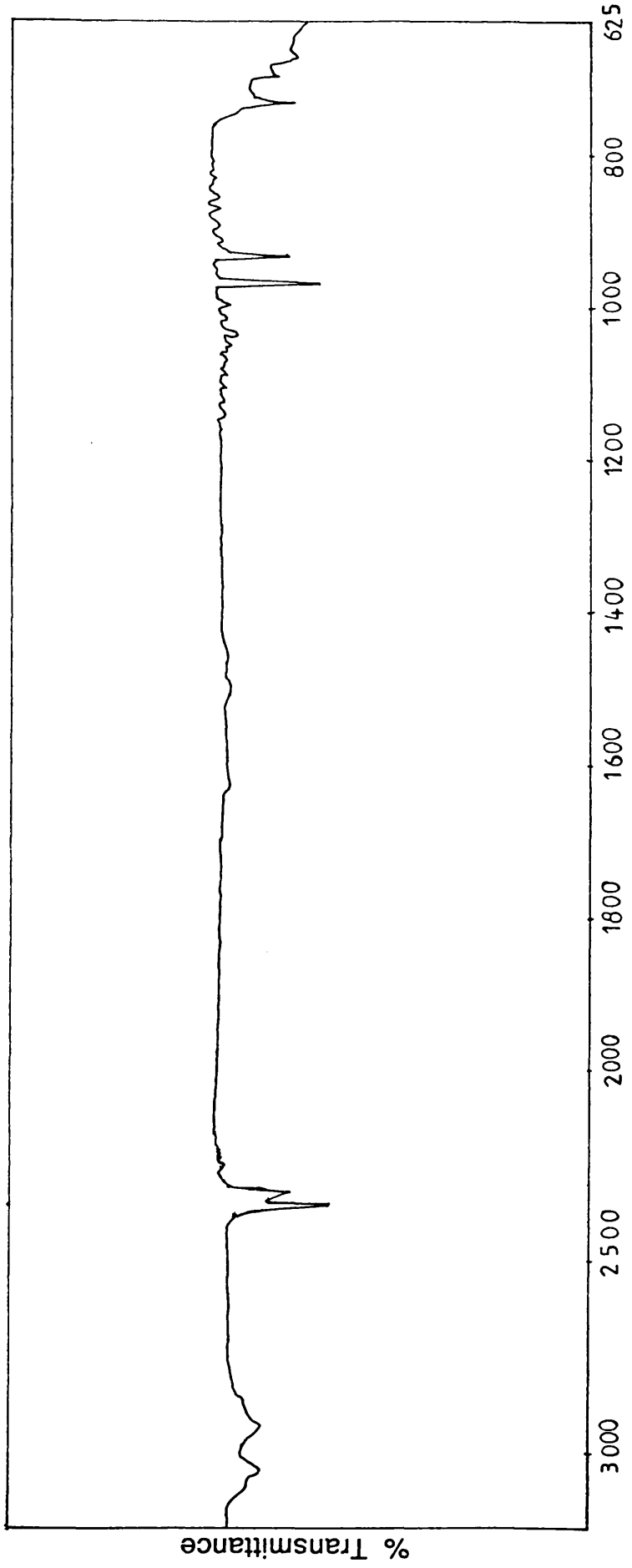


Fig. 8.7. Infrared spectrum of gaseous volatile products from degradation to 500 ^{o}C of amide linked block Polystyrene.

Table 8.6 Products Identified in the Cold Ring Fraction form degradation of ~~OC-PS-CONH$(CH_2)_6$NH~~ to 500 °C Under TVA Conditions.

Compounds	Name	Relative intensity	m/e
$H_2N(CH_2)_6NH_2$	1,6-diaminohexane	5.6	116
H_2N-CO-C(Ph)=CH_2	2-phenylacrylic-amide	4.7	147
H_2C(Ph)-CH_2-C(Ph)=CH_2	styrene dimer	15.8	208
H_3C-CH(Ph)-CH_2-C(Ph)=CH_2	dimer with extra methyl group	5.5	222
H_2N-CO-CH(Ph)-CH_2-CH_3	2-phenylbutyric acid amide	5.1	163
$H_2N(CH_2)_6$NH-CO-CH(Ph)-CH_2-C(Ph)=CH_2		3.4	350
$H_2N(CH_2)_6$-NH-CO-CH_2(Ph)		8.5	234
$H_2N(CH_2)_6$NH-CO-C(Ph)=CH_2		2.5	246

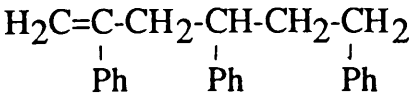
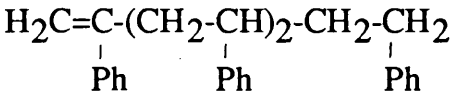
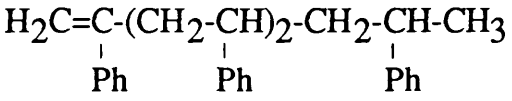
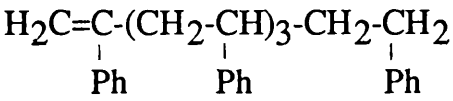
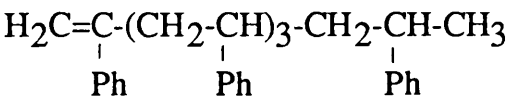
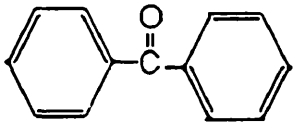
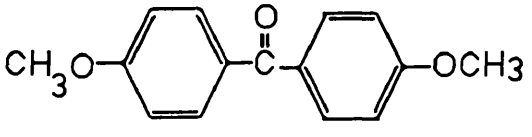
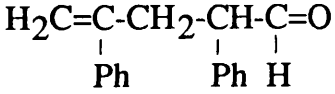
	styrene trimer	10.7	312
	styrene tetramer	2.7	416
	tetramer with extra methyl group	2.6	430
	styrene pentamer	1.7	520
	pentamer with extra methyl group	1.5	534

Table 8.7 Products Identified in Cold Ring Fraction form degradation of ~~OC-PS-CO-R~~ Using Programmed to 500 ^{o}C Under TVA Conditions.

Compounds	Name	m/e
H_2C(Ph)-CH_2-CH_2(Ph)	1,3-diphenyl propane	196
H_2C(Ph)-CH=CH(Ph)	1,3-diphenyl propene	194
	benzophenone	182
H_2C=C(Ph)-CH2-CH_2(Ph)	styrene dimer	208
H_2C=C(Ph)-CH_2-CH(Ph)-CH_3	dimer with extra methyl	222
	4,4-dimethoxybenzophenone	244
H_2C=C(Ph)-CH_2-CH(Ph)-C(OH)=O		252



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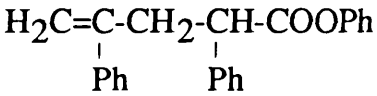

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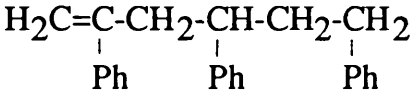
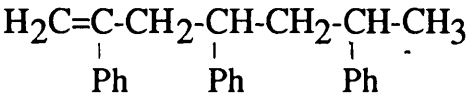


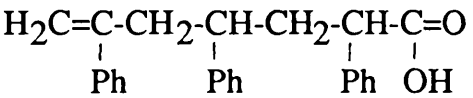
styrene trimer

312



trimer with extra methyl group

326



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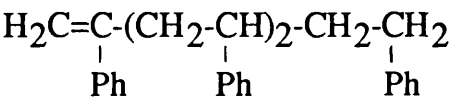
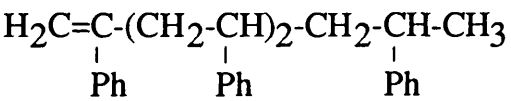


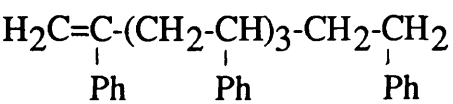
tetramer

416



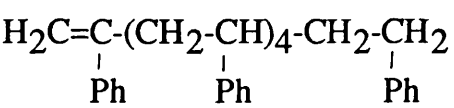
tetramer with extra methyl group

430



pentamer

520



hexamer

624

normal polystyrene, together with small amounts of -methylstyrene and benzene. The last fraction of the SATVA separation of degradation of ~~OC-PS-CONH$(CH_2)_6$NH~~ was also subjected to GC-MS and the chromatogram is illustrated in Fig. 8.9.

Toluene, α-methylstyrene, cyclopropylbenzene, phenylacetaldehyde and phenylpropionaldehyde are volatile products next in importance to styrene, using programmed heating. The degradation products are listed in Table 8.8 and 8.9.

2.2. THERMOGRAVIMETRY

The TG and DTG curves of the linked block polymers were obtained under dynamic nitrogen at heating rate of 10 ^{o}C/min are illustrated in Fig. 8.10(a,b).

The main decompositions appear at temperatures around 430^{o} and 412 ^{o}C. There was a 95% and 100% weight loss at 500 ^{o}C for ~~CO-PS-CONH$(CH_2)_6$NH~~ and ~~OC-PS-CO-R~~, respectively. Fig.8.10(a) indicates that weight loss begins at near 100 ^{o}C which is probably due to release of trace amount of solvent.

The results show that these linked block polystyrene samples are slightly more stable than dicarboxyl-terminated polystyrene and comparable in stability with normal polystyrene.

2.3. DIFFERENTIAL THERMAL ANALYSIS

The DTA curves, Fig. 8.11 for both linked block polymers were obtained , under nitrogen atmosphere in the range 25-485 ^{o}C. The curve shows a single endotherm. The main step of decomposition of ~~OC-PS-CONH$(CH_2)_6$NH~~ and ~~OC-PS-CO-R~~ polymer samples are observed at 428^{o} and 415 ^{o}C, respectively. The DTA, TG and DTG results are therefore consistent and are

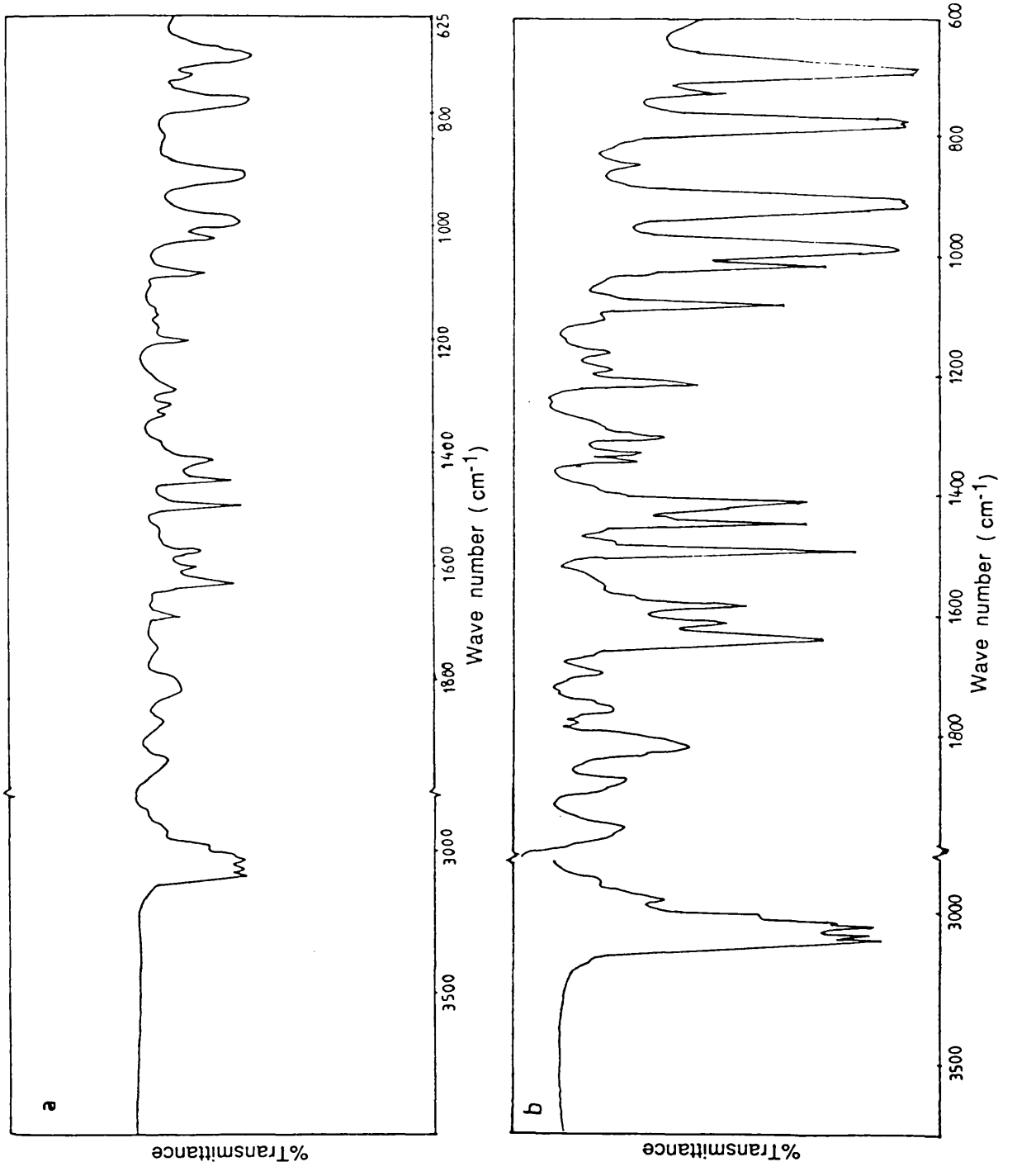


Fig. 8.8. Infrared spectra of liquid fractions from degradation to 500 ^{o}C of linked block Polystyrenes. (a) Amide (b) Ester.

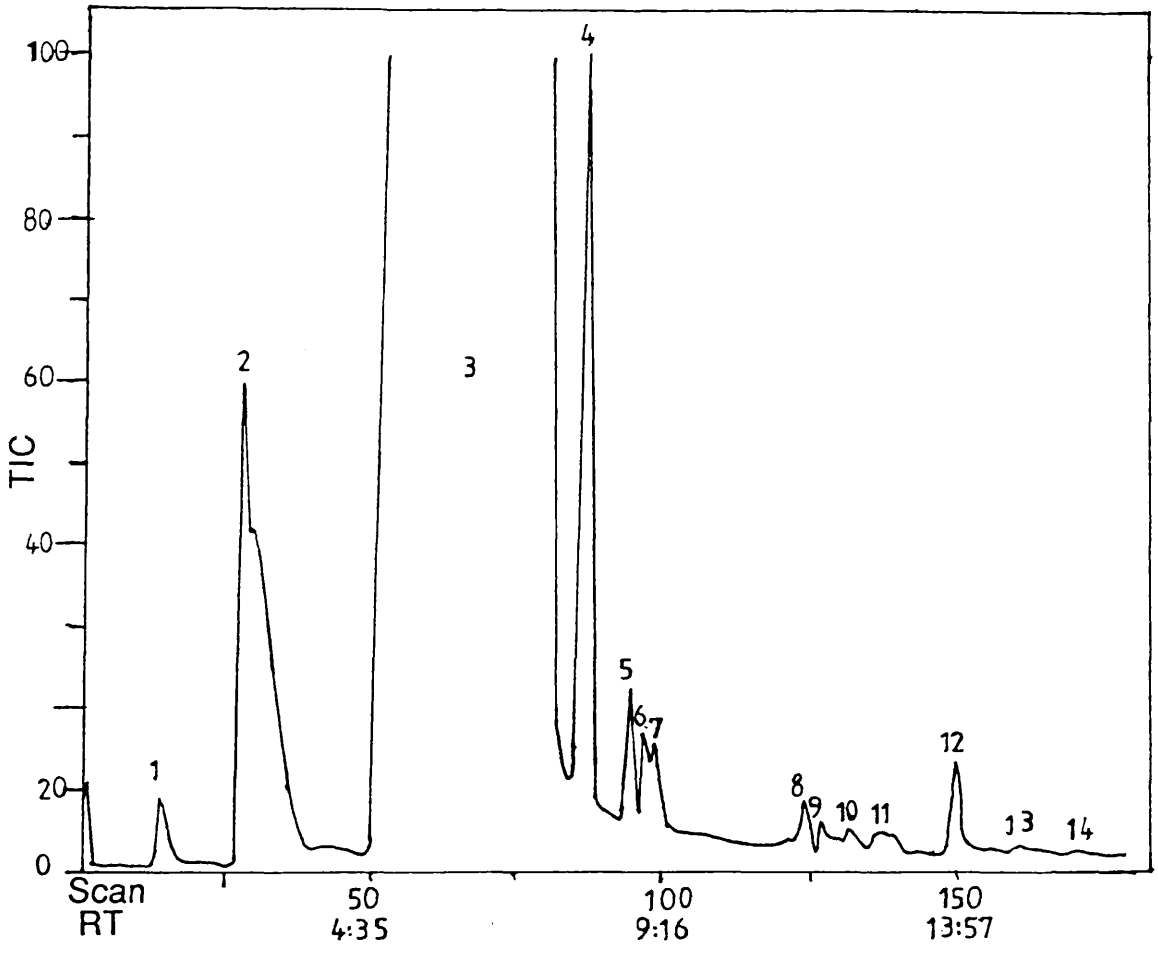


Fig. 8.9. GC-MS chromatogram for liquid fraction from degradation to 500°C of amide linked block Polystyrene.

Assignments: 1; Benzene, 2; Toluene, 3; Styrene, 4; ∝-methyl-styrene, 5; Allylbenzene, 6; Isopropylbenzene, 7; Cyclopropylbenzene,.8; Phenylpropanaldehyde, 9; Phenylacetaldehyde, 10; Unknown, 11; Acetophenone, 12; Naphthalene, 13 and 14; Unknown.

Table 8.8 Products of Degradation of ~~OC-PS-CONH$(CH_2)_6$NH~~ to 500 °C at 10 °C/min Under TVA Conditions.

Non-condensable products at -196 °C	Condensable volatile products at -196 °C			Cold Ring Fraction	Residue (Black)
	Gases	Liquid Fraction			
IR,MS	IR,MS	IR,MS	GC-MS	IR,MS	IR
*Carbon monoxide	*Carbon dioxide *Ammonia *Isocyanic acid Benzene Toluene	Styrene Toluene ∝-methyl styrene Benzene *Cyclopropylbenzene *Benzaldehyde Ethylbezene *Phenylacetaldehyde Phenyl-2-butene Allylbenzene Naphthalene *Acetophenone *Phenylpropionaldehyde	Styrene Toluene Benzene ∝-methyl styrene Allylbenzene *Isopropylbenzene *Cyclopropylbenzene *Phenyl propionaldehyde *Phenylacetaldehyde Naphthalene *Acetophenone	Short chain fragments containing carbonyl and amide groups	Ammonium salt

*Products not obtained from polystyrene.

Table 8.9 Products of Degradation of ~~OC-PS-CO-R~~ to 500 °C at 10°C/min Under Normal TVA Conditions.

Non-condensable products at -196 °C	Condensable volatile products at -196 °C		Cold Ring Fraction
	Gases	Liquid Fraction	
IR	IR,MS	IR,MS	IR,MS
*Carbon monoxide	*Carbon dioxide *Methanol Toluene	Styrene Toluene α-methyl styrene *Phenylacetic acid Benzene *Phenylbutane Phenylbutene *Phenylpropanoic acid Ethylbenzene Naphthalene Allylbenzene *Benzaldehyde	Mainly short chain fragments but some fragments containing carboxylate and carbonyl groups

*Products not obtained from polystyrene.

summarised in Table 8.10

3. MECHANISM OF DEGRADATION

The degradation behaviour of polystyrene and diacid chloride-terminated polystyrene has already been discussed in Chapters Five and Six, respectively.

The mechanism of degradation of polystyrene involves chain scission, depolymerisation to monomer, and both intra- and intermolecular transfer, the results of which have been described in Chapter Five. Below 300 ^{o}C, only chain scission and disproportionation of the macroradicals occur.

The mechanism of degradation of linked block polymers appears to be basically similar to that of normal polystyrene. Above 300 ^{o}C some additional volatile products were obtained. The suggested mechanisms of degradation of ~~OC-PS-$CONH(CH_2)_6NH$~~ and ~~OC-PS-CO-R~~ accounting for the additional products are shown in scheme 1 and 2, respectively.

4. CONCLUSIONS

There is no major change observed in the main decomposition temperature of the linked block polymer samples in comparison with that of the styrene homopolymer. This is as expected due to the small proportion of linking units.

The weight percentages of cold ring fraction in these polymers, however, are higher than for normal polystyrene. This is explained by additional backbone scission at the linking units and some reduction in the zip length of depropagation to monomer. The weight percentage of cold ring fraction in carboxyl-terminated polystyrene was also lower than in the linked block polymers.

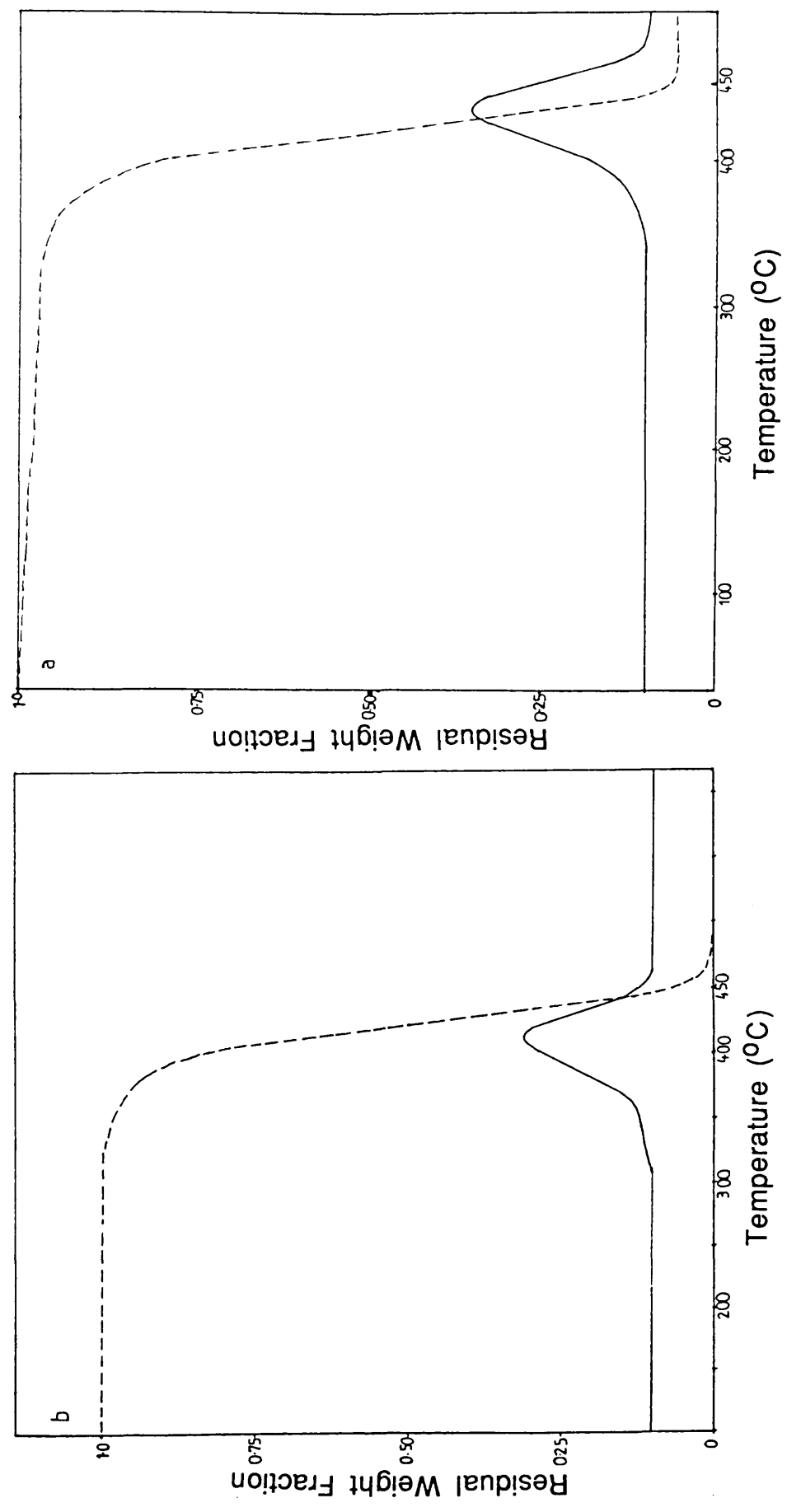


Fig. 8.10. TG and DTA curves for linked block Polystyrenes.
(a) Amide (b) Ester Keys: _ _ _ TG, ___ DTG.

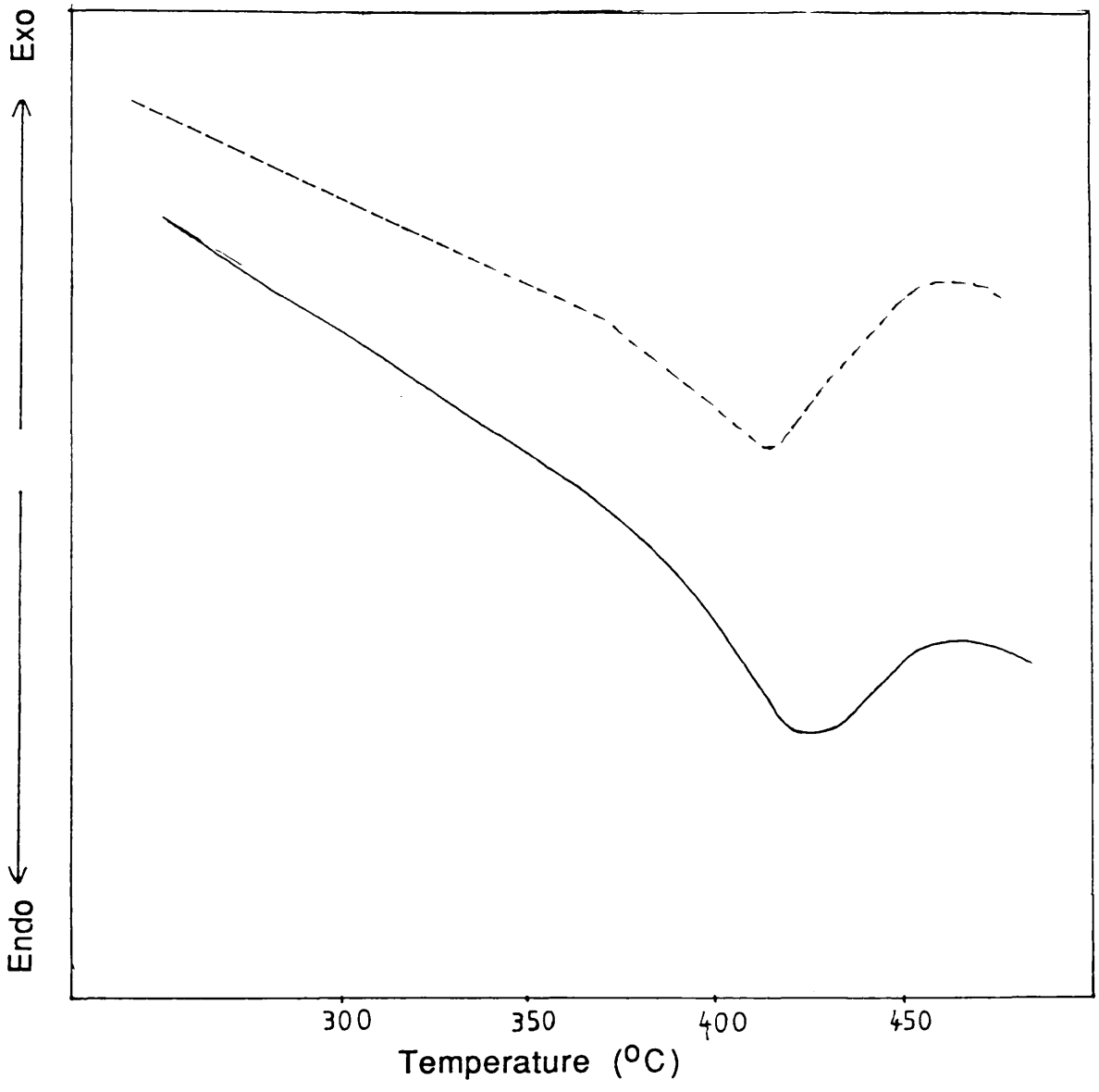


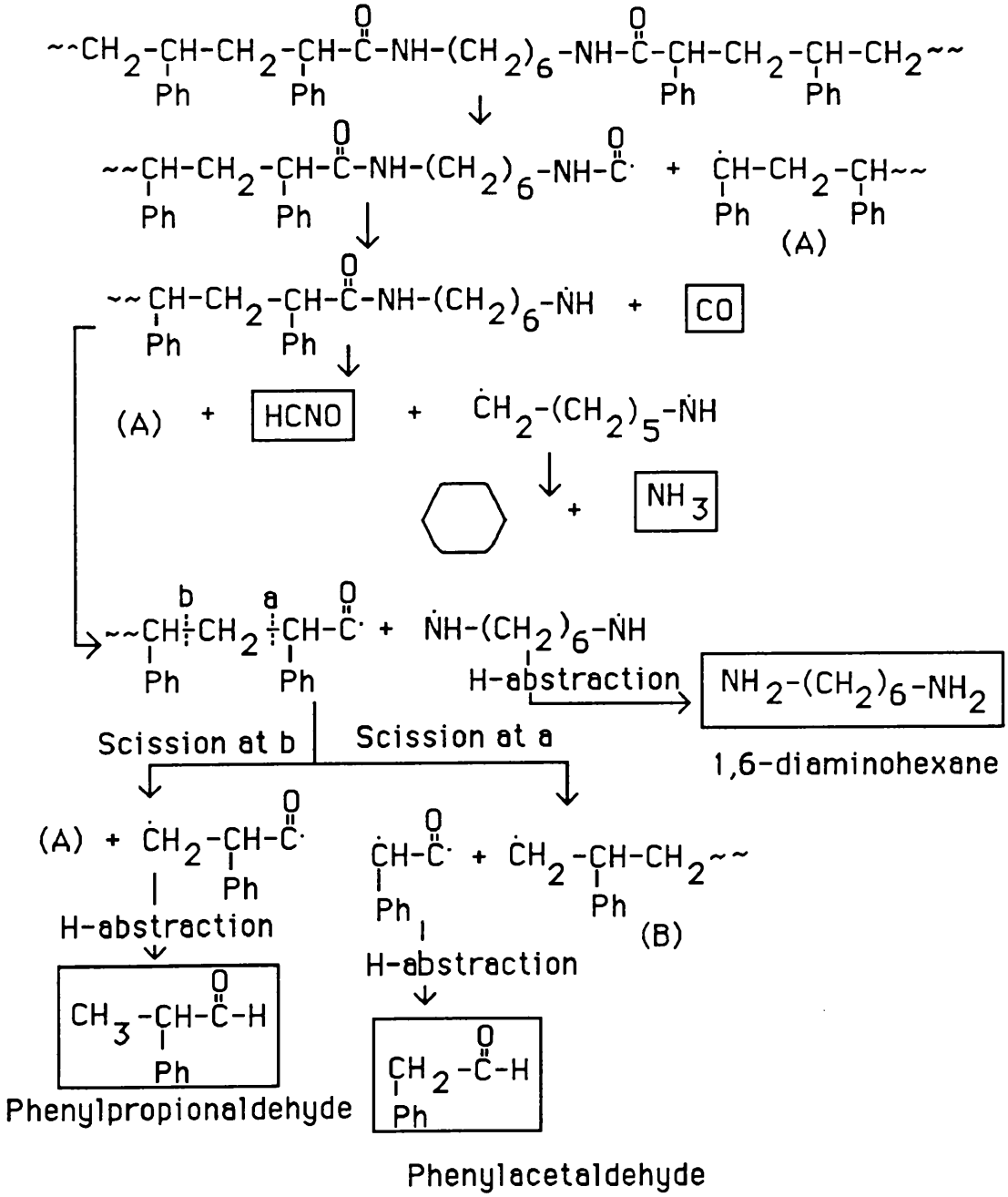
Fig. 8.11. DTA curves for linked block Polystyrenes under dynamic nitrogen at 10 °C/min to 500 °C.

Keys: ___Amide _ _ _ Ester

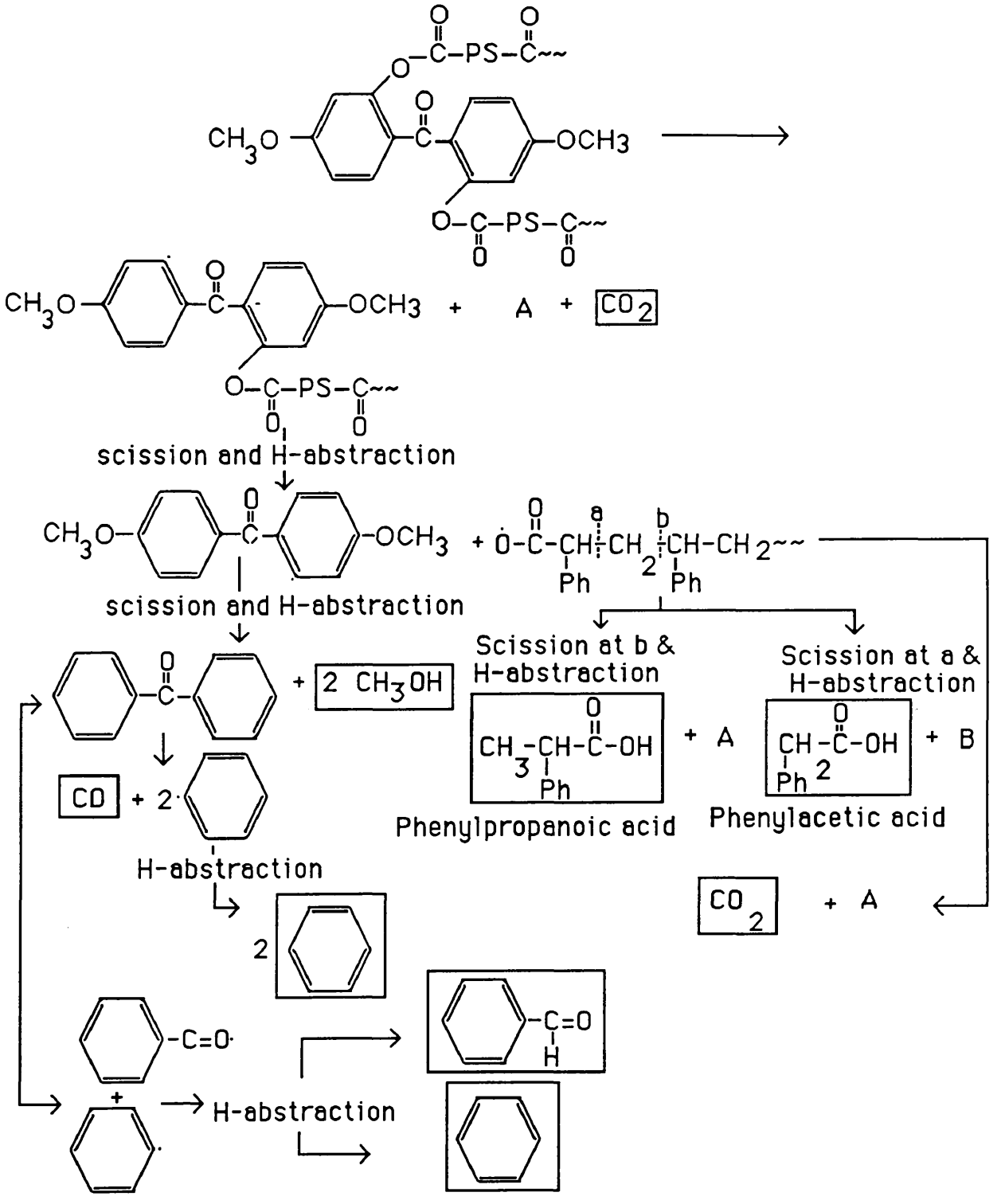
Table 8.10 DTG, TG and DTA Data for ~~OC-PS-CONH$(CH_2)_6$NH~~ and ~~OC-PS-CO-R~~ Samples Under Programmed Heating at 10 ^oC/min in Nitrogen.

Polymer	DTG		TG		DTA	
	Peak temp., ^oC	Temp. range, ^oC	1%wt. loss, at ^oC	50%wt. loss, at ^oC	peak temp., ^oC	Thermal effect
~OC-PS-CONH$(CH_2)_6$NH~	430	340-480	275	412	428	Endo.
~~OC-PS-CO-R~~	412	312-470	320	390	415	Endo.

Scheme 1 Mechanism of Formation of Minor Products from Chain Ends in Degradation of ~~CO-PS-CONH(CH_2)$_6$NH~~



Scheme 2 Mechanism of Formation of Minor Products from Chain Ends in Degradation of ~~CO-PS-CO-R ~~



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